Tracing the Evolution of Ice and Organics: From Interstellar Ice Grains to Evolved Solar System Icy Bodies

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Workshop on Interstellar Matter, Sapporo; Nov 14-16, 2018

My Motivation

Evolution of Organic Matter in a

Planetary System

Leading to Potential Origin of Life

And

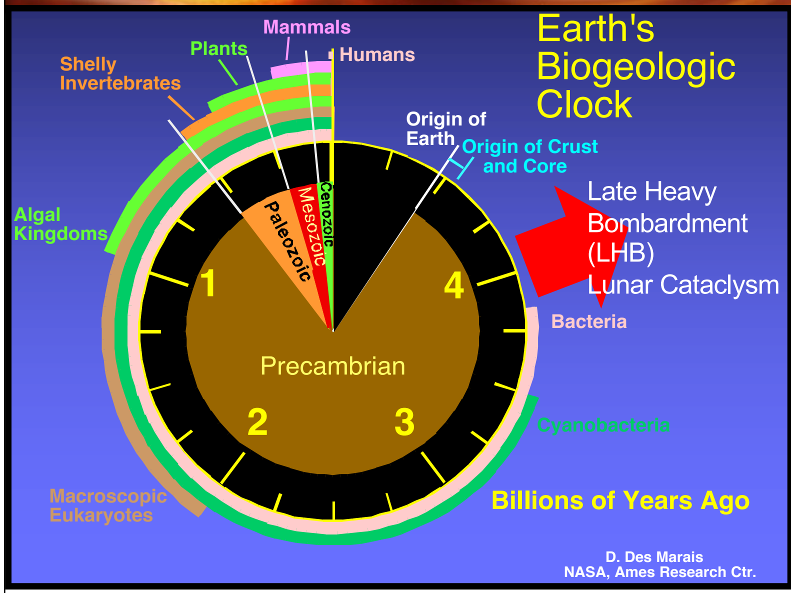
Habitability beyond Earth

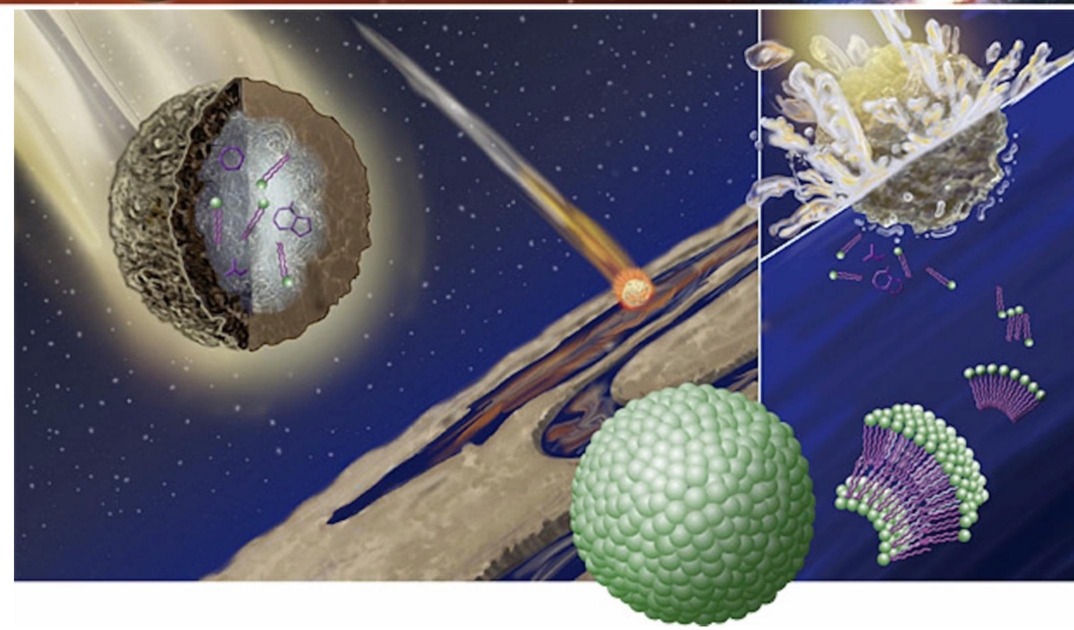
Part I: From Interstellar to Comets

Can Present-Day Comets Carry Primordial Material?
How can we “Trace” back through more than 4.6 BY?

Can there be ”Tracer Phenomena” or “Tracer Species” (Tracers) that we can use to follow back in Time?

Earth, Comets & Asteroids, and Origin of Life

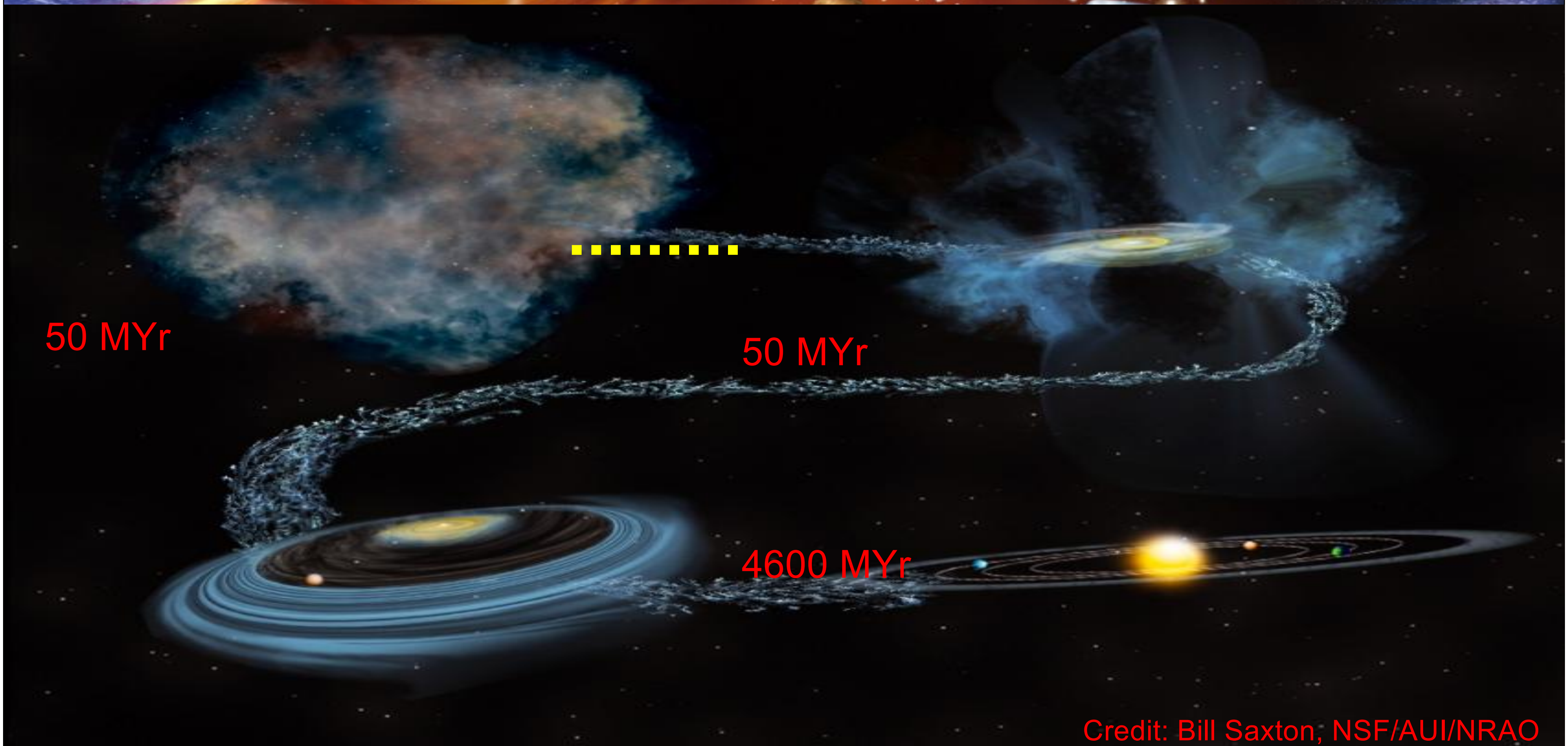




The Road is long and the Journey has just began to understand the Origin of Life on Earth!

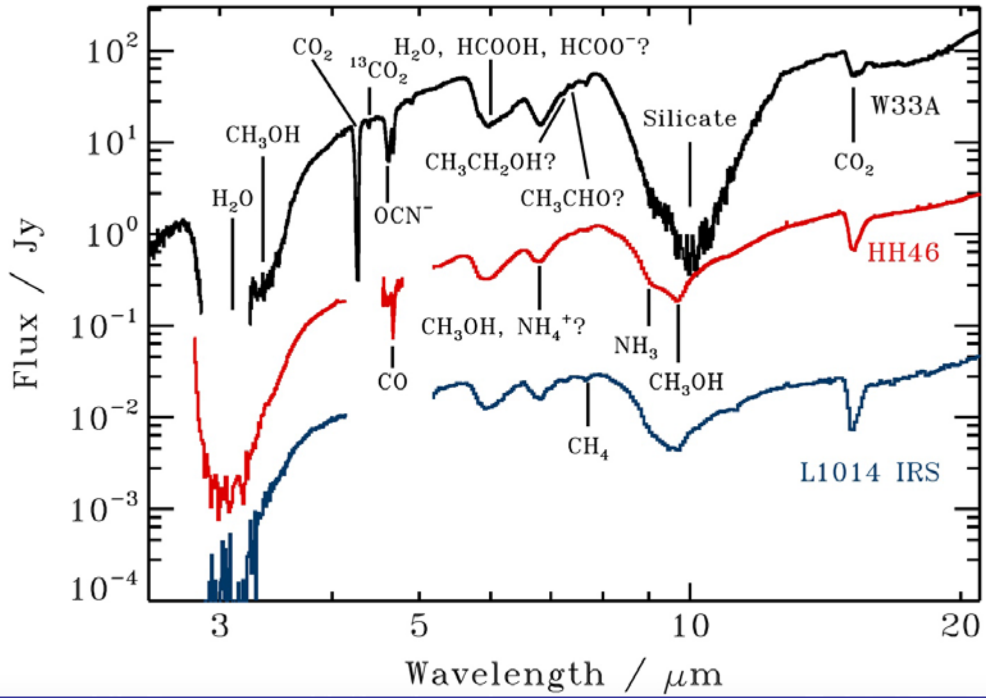
"Prebiotic Molecular Delivery" by Comets and Asteroid Precursors some 4 Billion Years ago to Earth, could have possibly triggered the "Origin of Life on Earth"

Stellar Evolution: “Tracers” Connecting the Dots…

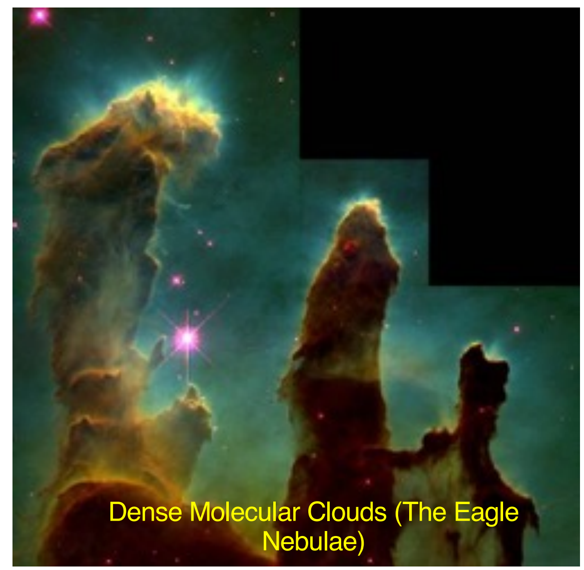


Amorphous Interstellar Ices

THE ASTROPHYSICAL JOURNAL, 740:109 (16pp), 2011 October 20
Boogert et al.



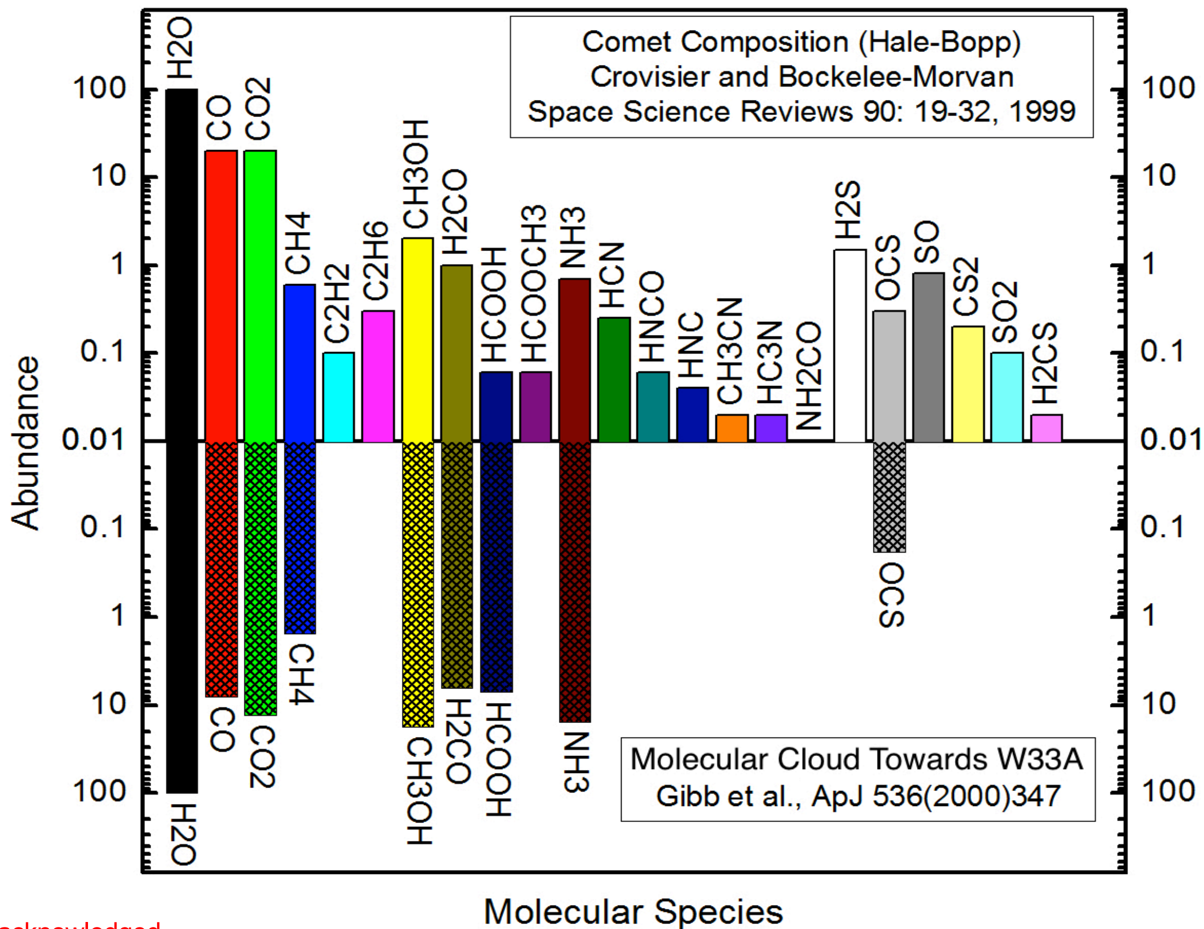
Oort Cloud Comets – Similar Composition?



Strikingly Similar Composition: Oort Cloud Comet(s) and Interstellar Ice Grains

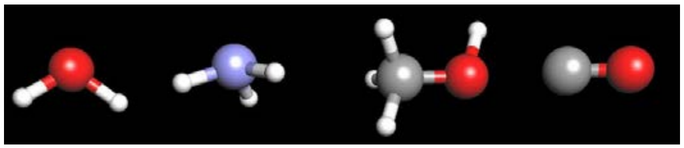
Is Cometary Nucleus a living Fossil of Interstellar Ice Grains?

Is Cometary Ice Amorphous or Crystalline?



Energy: Not Too Much Please!

Cryogenic Cosmic Ices

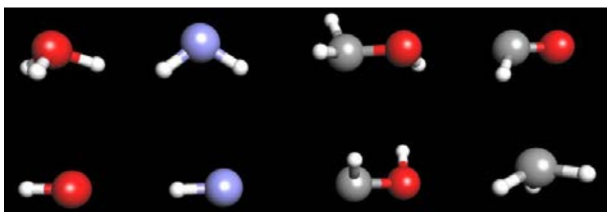


Raw Material
H_2O, NH_3, CH_3OH, CO

Photons/Electrons
Cosmic Rays
Debris/Collisions

Temperature

Radicals, Ions, Electrons, & Molecules

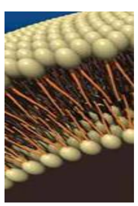


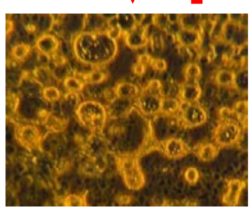
Building Blocks
Atoms, Radicals & Ions

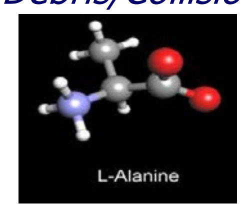
Temperature

Photons/Electrons
Cosmic Rays
Debris/Collisions

Amino Acids, Micelles, etc.







Biomolecules
Amino Acids etc.

Energy is essential to drive Chemistry: From Simple to Complex!

But too much of Energy can destroy Complex Molecules!

Complex Organic Molecules in ISM to COmets

Energy (Photons, Electrons, Ions, etc.,)

+

Simple Ice (H_2O, NH_3, CH_3OH) @ 5 K

=

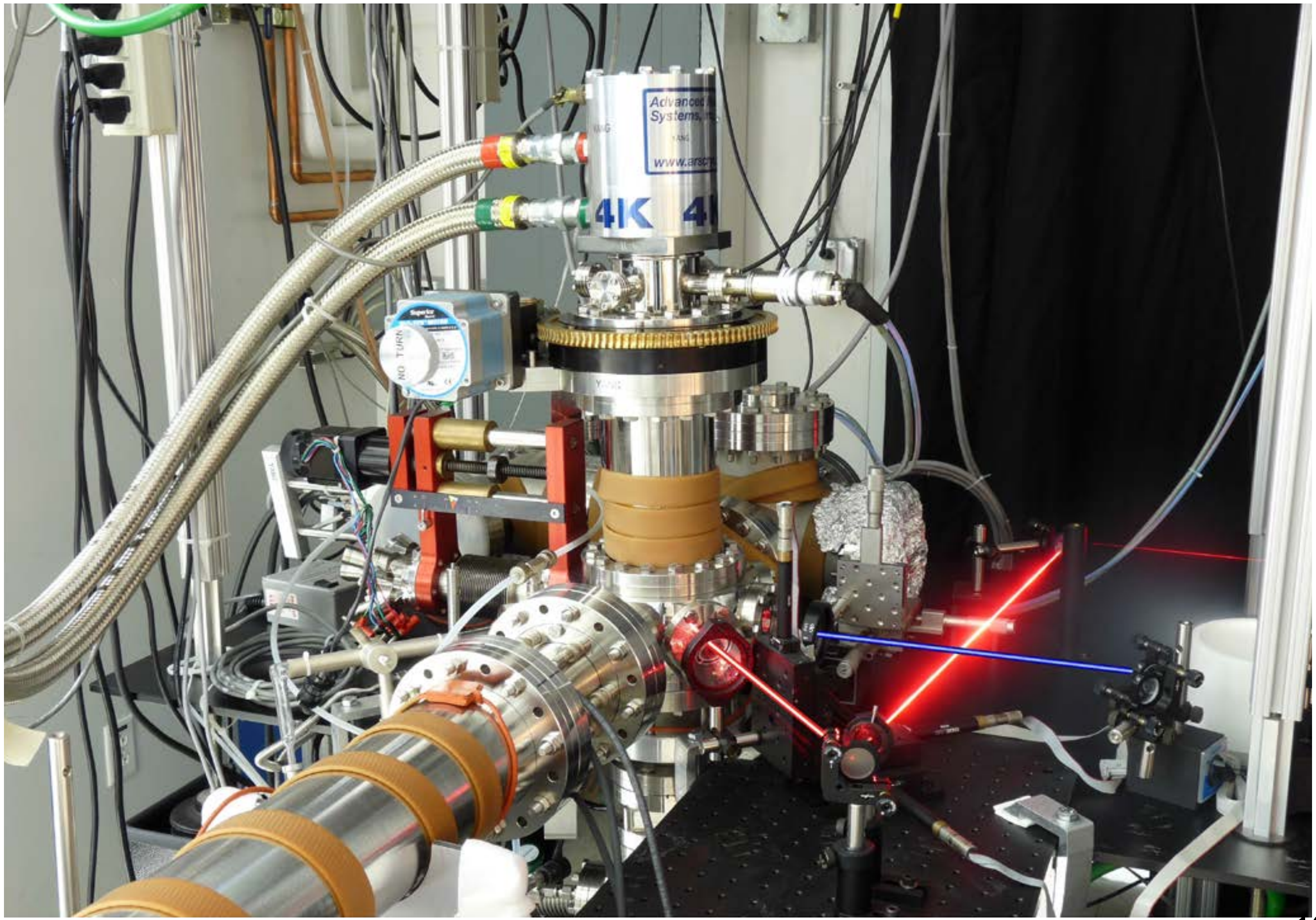
Complex Organic Molecules (Interstellar & Cometary)

Understanding Prebiotic Chemistry in ISM & Comets

At the Ice Spectroscopy Lab (ISL) @ JPL

Two-Color, Two-Step, Laser-Ablation & Laser-Ionization Time-of-Flight Mass Spectrometry

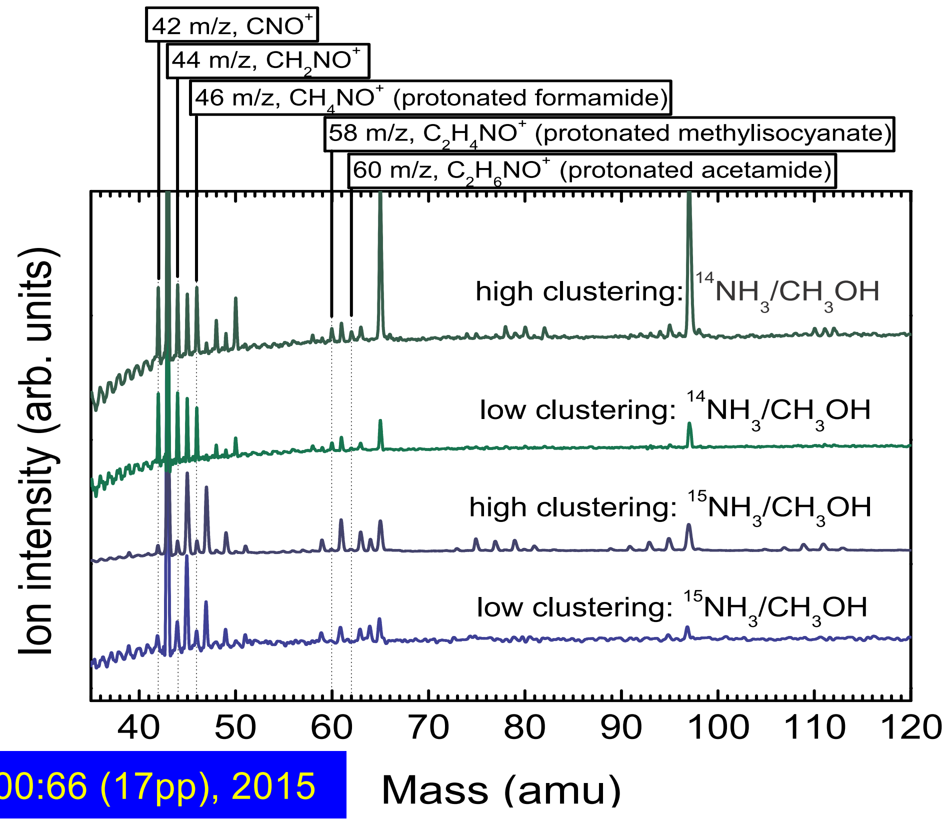
Analyzing Ice Composition in One Scoop!



Radiation Chemistry of $H_2O/CH_3OH/NH_3$ Ice

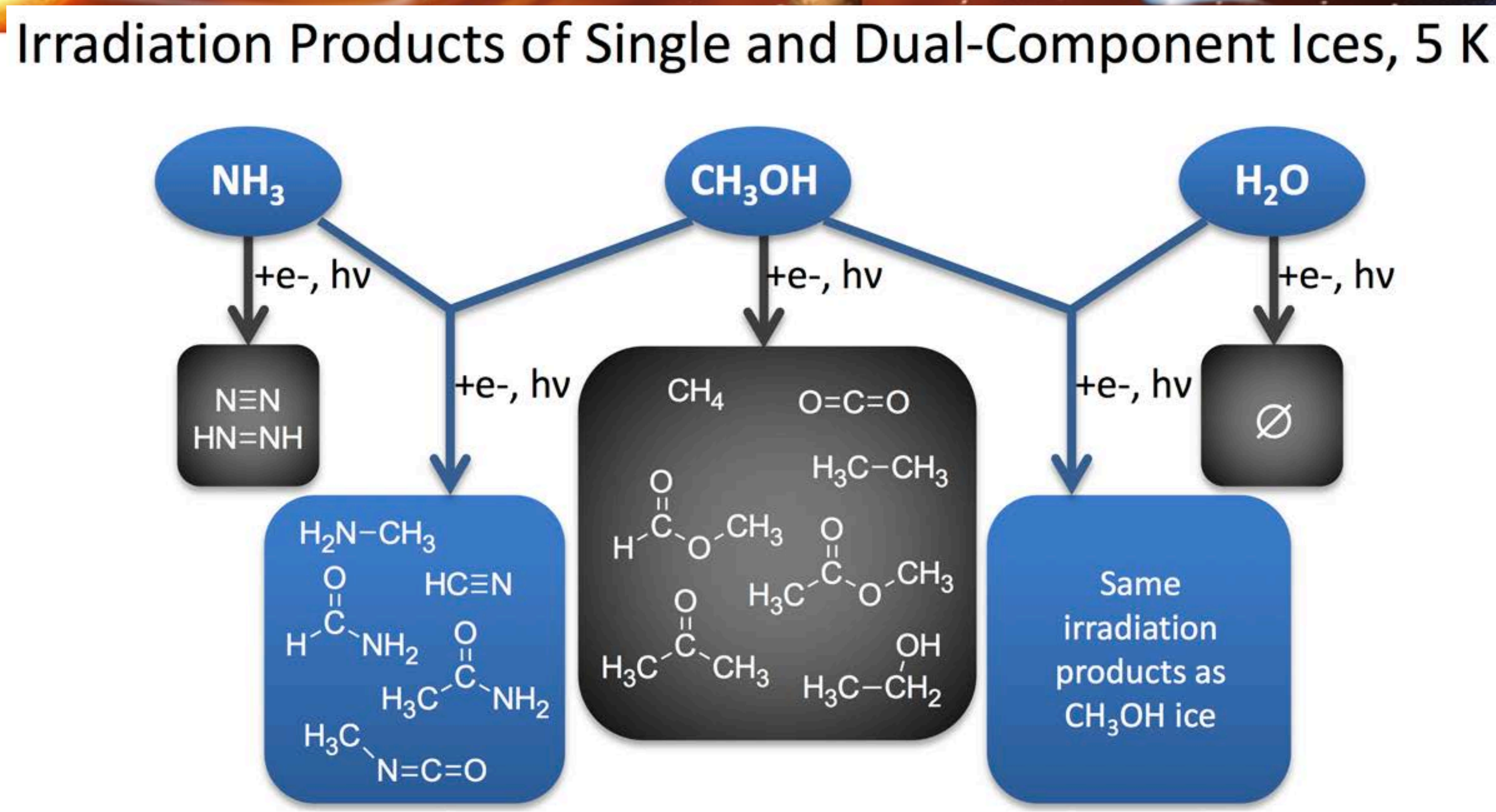
Snapshots/Scooping the Evolution of Astrophysical Ice Analogs

Interstellar / Cometary Ice Analogs Produce Key Building Blocks Of Life upon Radiation Processing



Henderson and Gudipati ApJ - 800:66 (17pp), 2015

Molecules found in interstellar ice analogs



Many of these molecules are detected by Rosetta-ROSINA

NH_3 less reactive than CH_3OH under radiation

Rosetta Observations

Table 1. Parent molecules used for fitting the COSAC spectrum according to Goesmann et al. (2015). Species in bold have never before been identified in a comet. The last column indicates which of the molecules have been identified in the ROSINA–DFMS spectra during the 2016 September 5 event.

Molecule		Mass (Da)	Rel. abundance (per cent)	Identified in DFMS spectra
CH_4	Methane	16	0.7	Y
H_2O	Water	18	80.9	Y
CHN	Hydrogencyanide	27	1.1	Y
CO	Carbon monoxide	28	1.1	Y
CH_5N	Methylamine	31	1.2	Y
CH_3CN	Acetonitrile	41	0.5	minor
CHNO	Isocyanic acid	43	0.5	Y
C_2H_4O	Acetaldehyde	44	1.0	Y
CH_3NO	Formamide	45	3.7	Y
$C_2H_5NH_2$	Ethylamine	45	0.7	Y
CH_3NCO	**Methyl isocyanate**	57	3.1	
C_3H_6O	**Acetone**	58	1.0	Y
C_2H_5CHO	**Propanal**	58	0.4	?
CH_3CONH_2	**Acetamide**	59	2.2	minor
CH_2OHCHO	Glycol aldehyde	60	1.0	
$CH_2(OH)CH_2(OH)$	Ethylene glycol	62	0.8	Y

Altwegg et al., MNRAS 469, S130–S141 (2017)

When and Where Complex Organics are formed?

Tracing the Origins of Complex Organics needs "TRACER" Molecules

Primordial or Constantly Evolving?

Dense Molecular Clouds – Formation & Lifetime ~50 Myr (10K)

Protoplanetary Pebbles & Cometesimals – ~50 Myr (10 – 130 K)??

KBO Precursors – Scattered out by Saturn & Jupiter (Warmer?) (~30 K)

Rest of 4600 Myr – Hibernation/Cosmic Rays in KBO Region? (~30 K)

Centaur – A few Myrs (~50 K – 100 K)

Today's Short Period Comets – A few Hundred Years?? (120 K – 350 K)

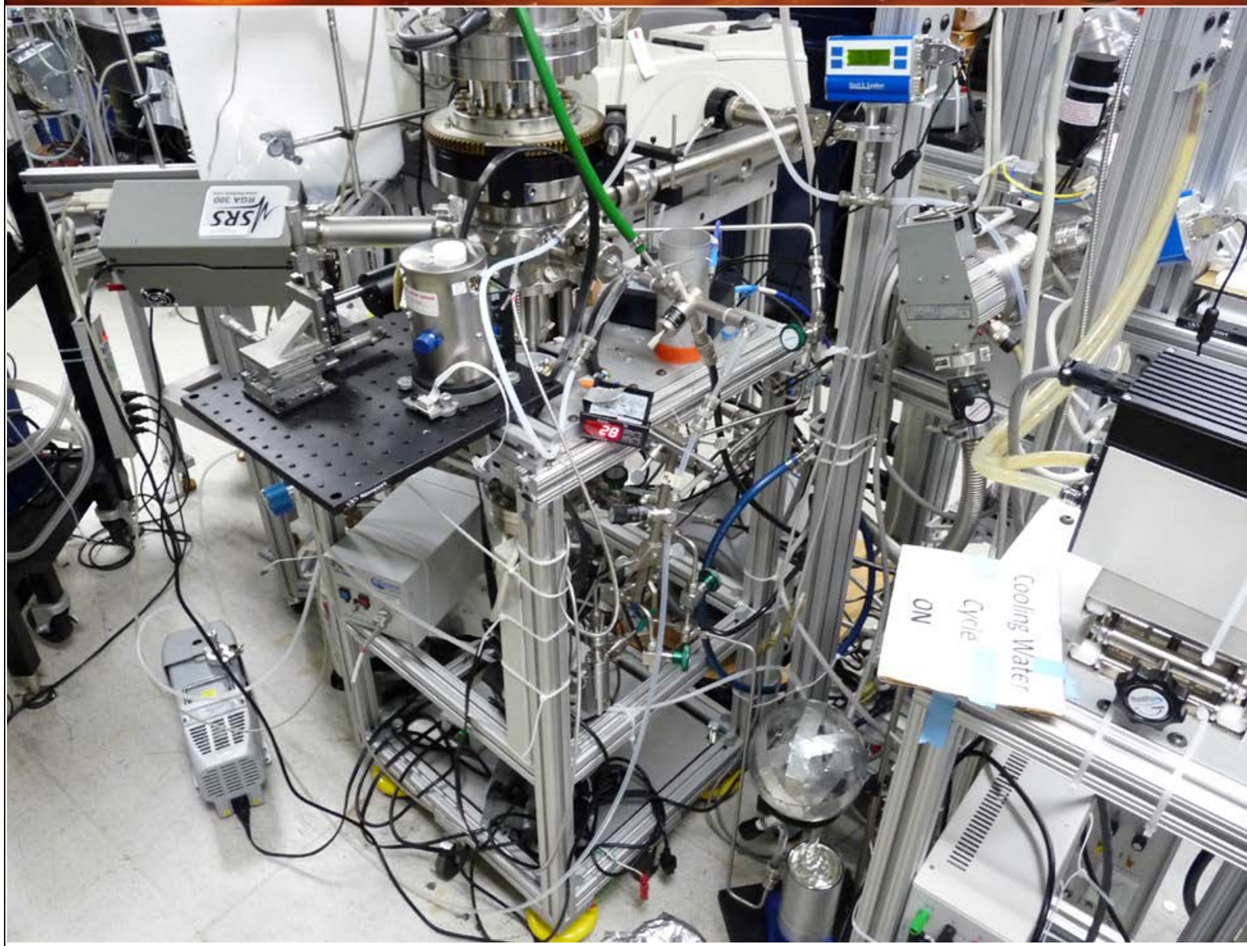
Source of Energy: Cosmic Rays, UV, and Non-Thermal

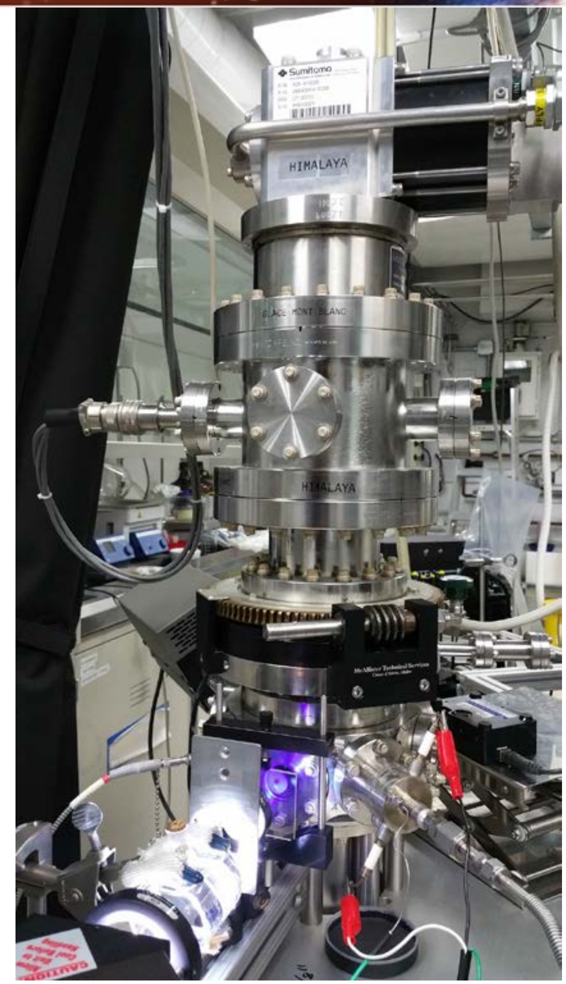
Can Tracers connect today's Cometary Material to Primordial Composition
4 Billion Years Ago?
If not, the Story is only half-complete!

Tracer No. 1 – Amorphous Ice

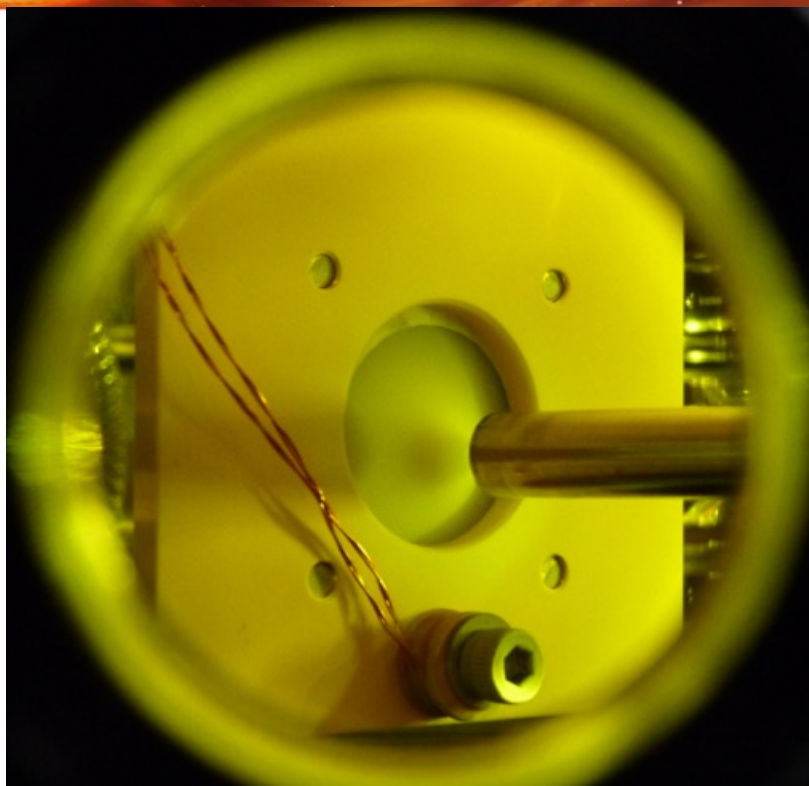
- We know: Interstellar ice grains contain **amorphous water ice**
- We do not know: A comets interior ice phase: **Amorphous or Crystalline?**
- We need to **"Dig Deep" into a Comet and bring back unaltered sample at <25 K** to resolve this Key Question.

Work at the Ice Spectroscopy Laboratory (ISL) at JPL

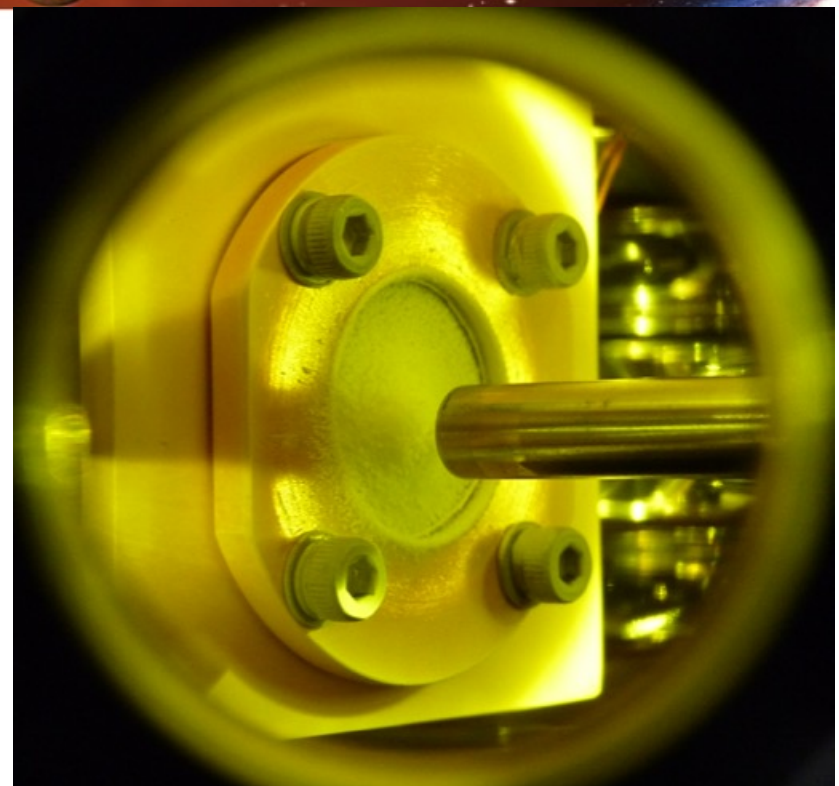




Macroscopic Amorphous Ices in the Lab: Simulating Interstellar & Comet Ices

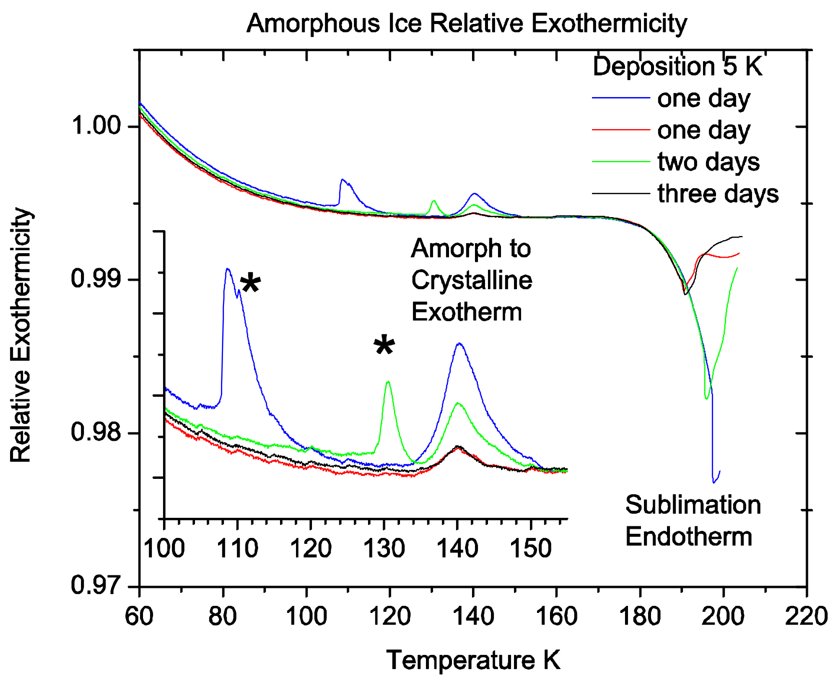


150 K Deposition
(Crystalline)



5 K Deposition
(Amorphous)

Amorphous to Crystalline – Exothermicity



Robert Wagner and Murthy Gudipati (2013) to be published

Impurities may change exothermic to endothermic (amorphous to crystalline) transition – Kochi & Sirono, GRL 28(2001) 827.

Kochi & Sirono GRL 28(2001)827

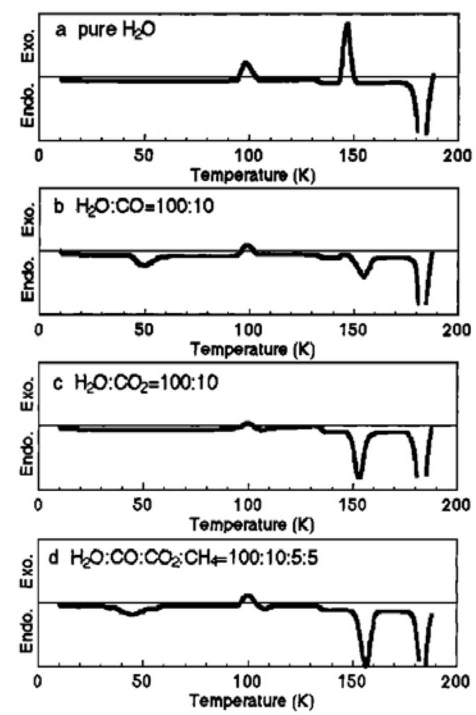
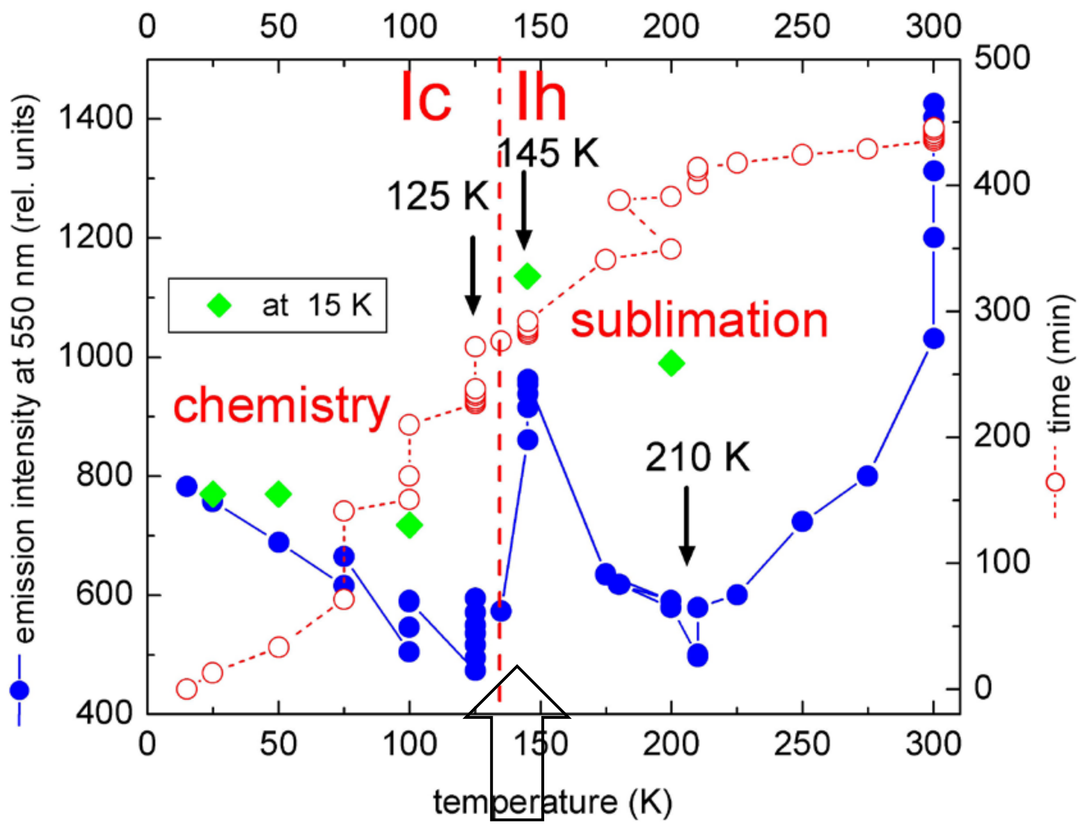


Figure 2. DTA curves of pure (a) and impure (b-d) a-H_2O. Endo., endothermic; Exo., exothermic.

Transitions in Amorphous Ices: Through Mobility of Reactive Species

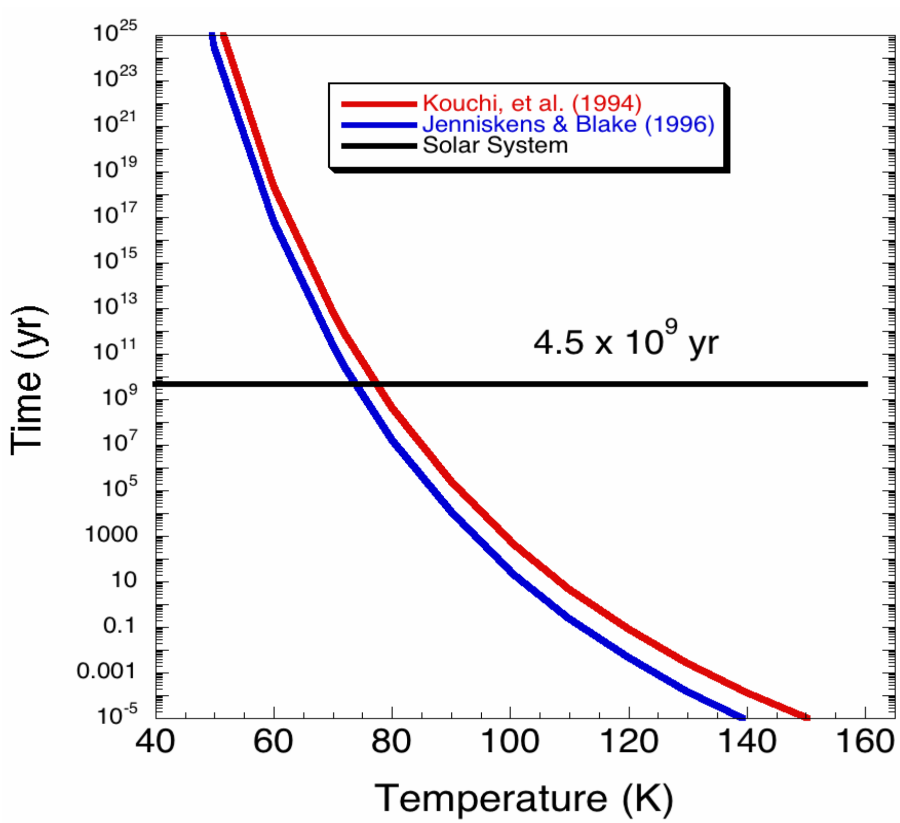
$H_2O:CH_3OH:NH_3:CO$ (100:50:1:1)



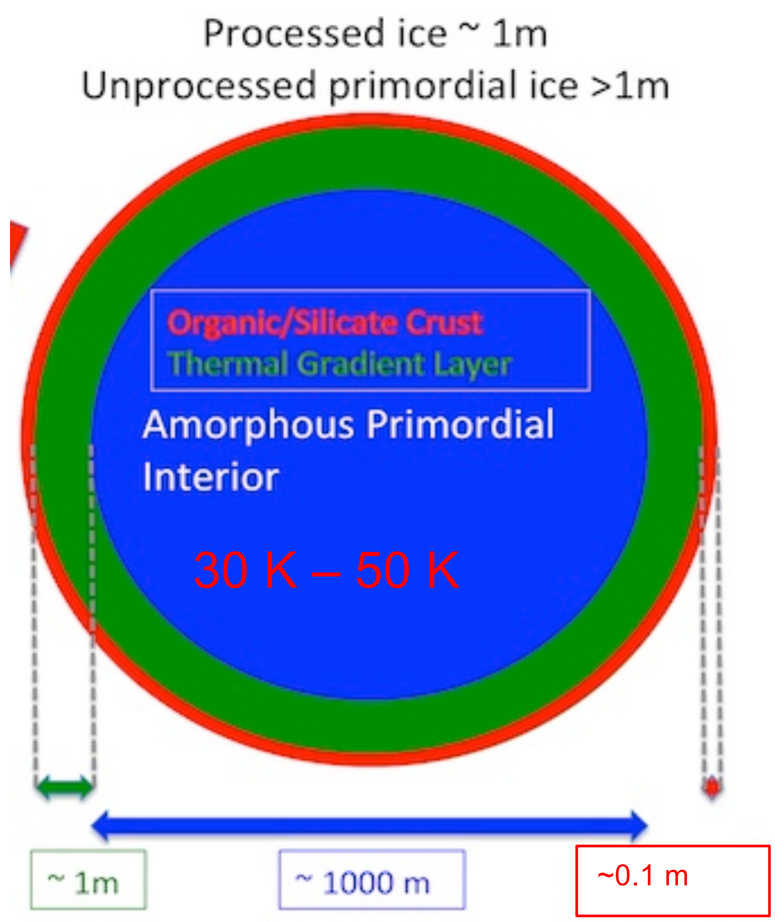
Amorphous Ice undergoes violent molecular motion at 120-150 K, leading to irreversible changes in ice composition, followed by Crystallization.

Gudipati et al., ApJ 583_514-523_2003

How Primitive is a Comet's Interior?



Mastrapa, Grundy, Gudipati (Solar System Ices 2013)



Future Cometary Missions!

Cryogenic Cometary Nucleus Interior Sample Return Mission will resolve this fundamental question. Perhaps not in my Lifetime!

Tracer 1: Amorphous Ice in Comets

Unless we "Dig Deep" into a Comet And Determine Whether OR NOT It's Interior is made of Amorphous Ice, We haven't fully connected the DOTs…

✔ Amorphous H_2O Ice Excellent Tracer

Tracer No.2: CO_3 and O_3

CO_2 is up to 20% of H_2O

Can form Separate CO_2 Ice Domains

Tracers from CO_2 Ice

- CO_2 is the second most abundant molecule (Interstellar & Cometary)
- If CO_2 is >>5%, it starts forming aggregates
- If CO_2 is >>10% it start forming pure ice domains
- Interstellar ice has CO_2 >>10%, hence Pure CO_2 domains must exist in interstellar ice grains.
- CO_2 Amorphous → Crystalline ~40 K

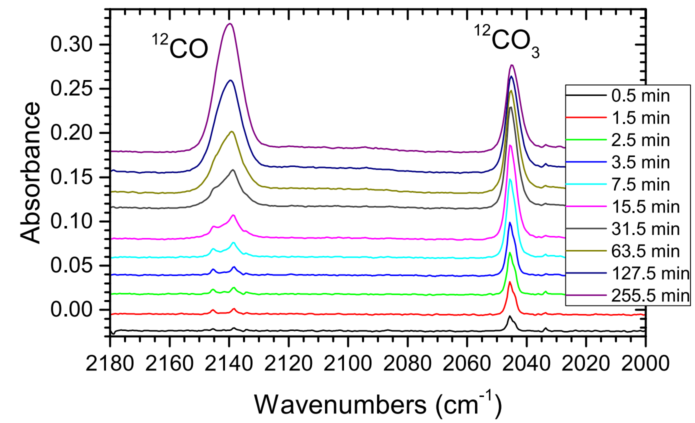
Let's see what is going on with CO_2 Ice

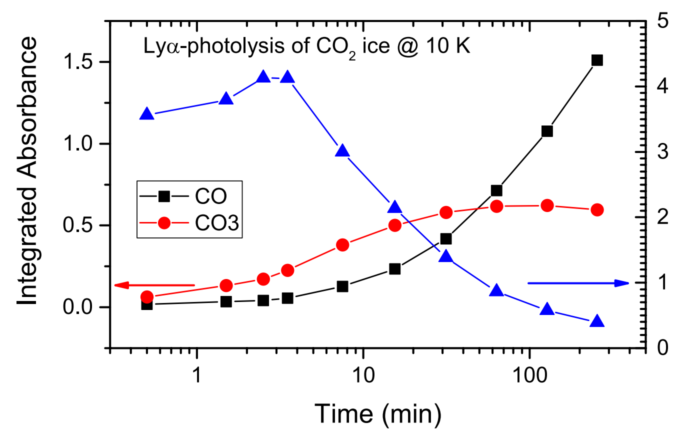
Photochemistry of CO_2/H_2O Ice

Soumya Radhakrishnan, Murthy S. Gudipati, et al. (ApJ 2018)

Pure CO_2 ice Irradiation Yields CO, CO_3, and O_3.

If CO_2 were to exist as pure ice (which it should be at >10% of H_2O) in the Interstellar Ice, then it should have produced CO_3 and we should see CO_3 if Cometary Interior is Primordial.





CO_2/H_2O Mixed Ice

With increasing H_2O content CO_3 and O_3 decrease. Pure CO_2 ice is a must!

More O_2 and O_3 is produced in CO_2 than in H_2O Ice

$CO_2 \rightarrow CO + O$

$CO_2 + O \rightarrow \mathbf{CO_3}$

$CO_3 \rightarrow CO + O_2$

$CO_3 \rightarrow CO_2 + O$

$O + O \rightarrow \mathbf{O_2}$

$O_2 + O \rightarrow \mathbf{O_3}$

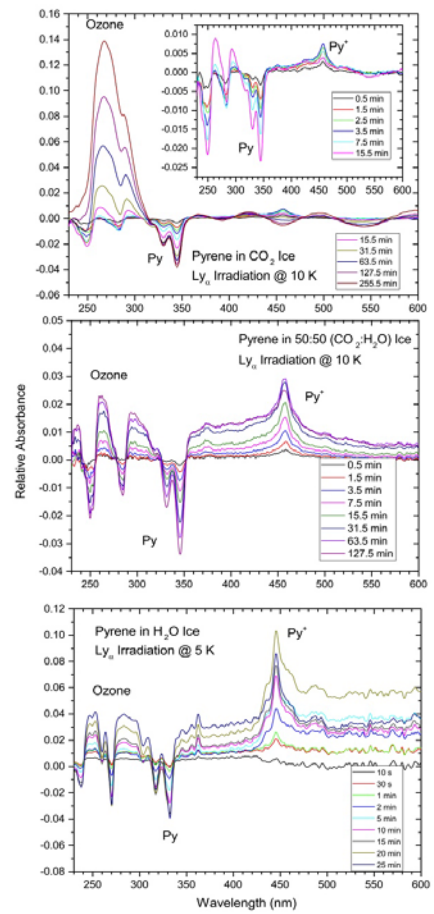
$O_3 \rightarrow O_2 + O$

$H_2O \rightarrow HO + H$

$HO + O \rightarrow \mathbf{HO_2}$

$H_2O + O \rightarrow \mathbf{H_2O_2}$

$\mathbf{O + O + O \rightarrow O_3}$



Tracer No.2: CO_3 is a good Tracer

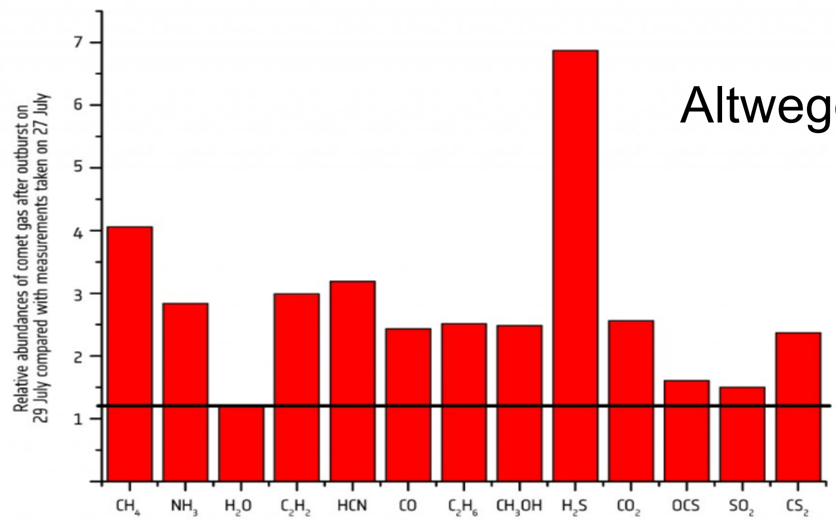
- If Protoplanetary Disk is a Washing Machine, CO3 should be gone!
- We should look for CO3 in Cometary Interior/Outgassing!

✔ **CO_3 is a good TRACER Molecule**
How about O_3??

Tracer No. 3: Trapped Supervolatiles in H_2O-Ice or CO_2-Ice

During Outbursts from Interior CO_2 is accompanied by Volatiles

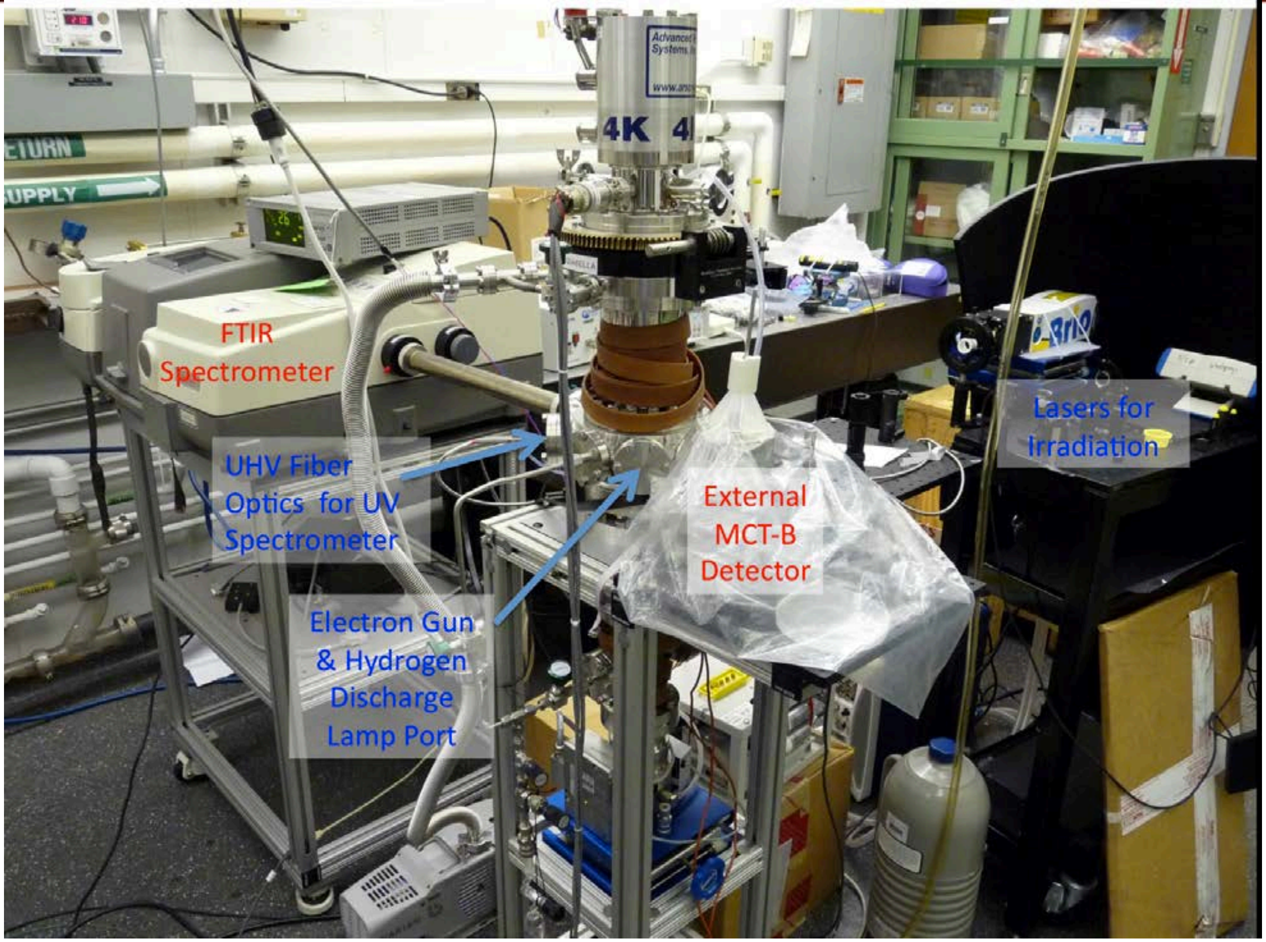
→ ROSINA MEASUREMENTS OF COMET GAS FOLLOWING OUTBURST



Altwegg et al.,

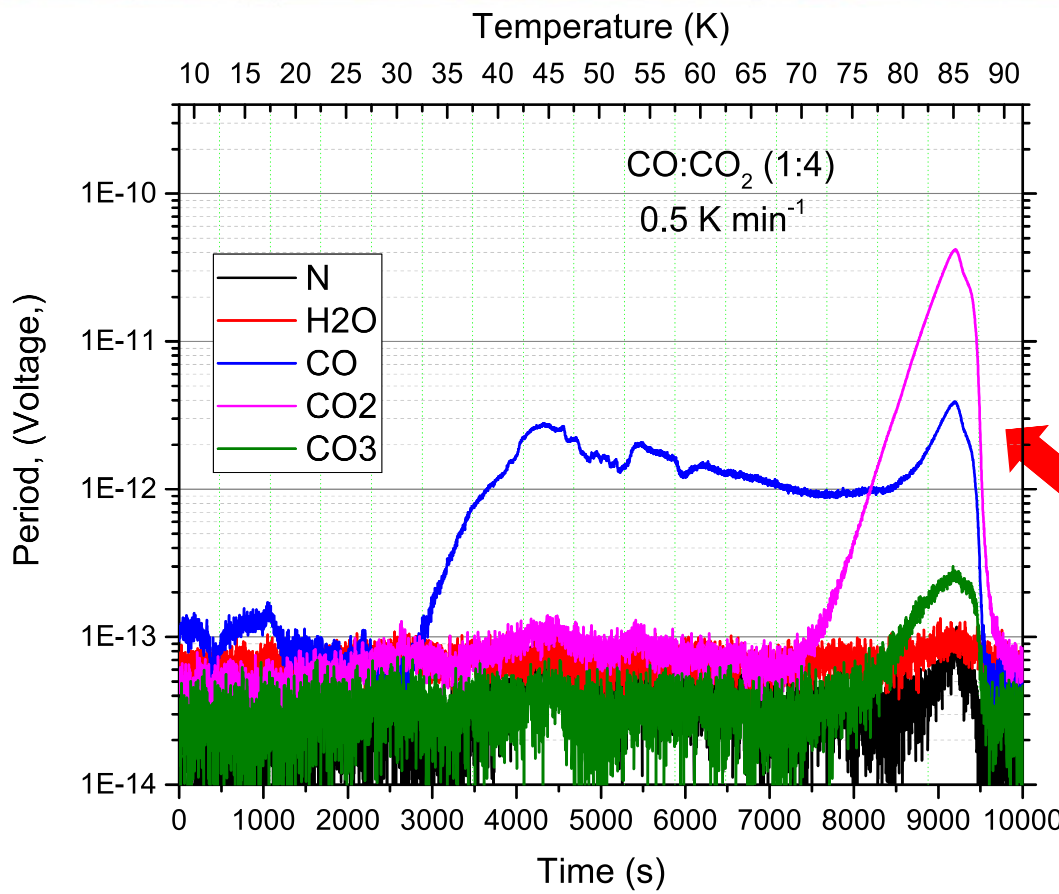
During an outburst of gas and dust from Comet 67P/Churyumov–Gerasimenko on 29 July 2015, Rosetta's ROSINA instrument detected a change in the composition of gases compared with previous days.
The graph shows the relative abundances of various gases after the outburst, compared with measurements two days earlier (water vapour is indicated by the black line).
Credits: ESA/Rosetta/ROSINA/UBern/ BIRA/LATMOS/LMM/IRAP/MPS/SwRI/TUB/UMich

Laboratory Studies at ISL of JPL



TPD and FTIR Spectroscopy of Cometary Ice Analogs

CO in CO_2 Ice

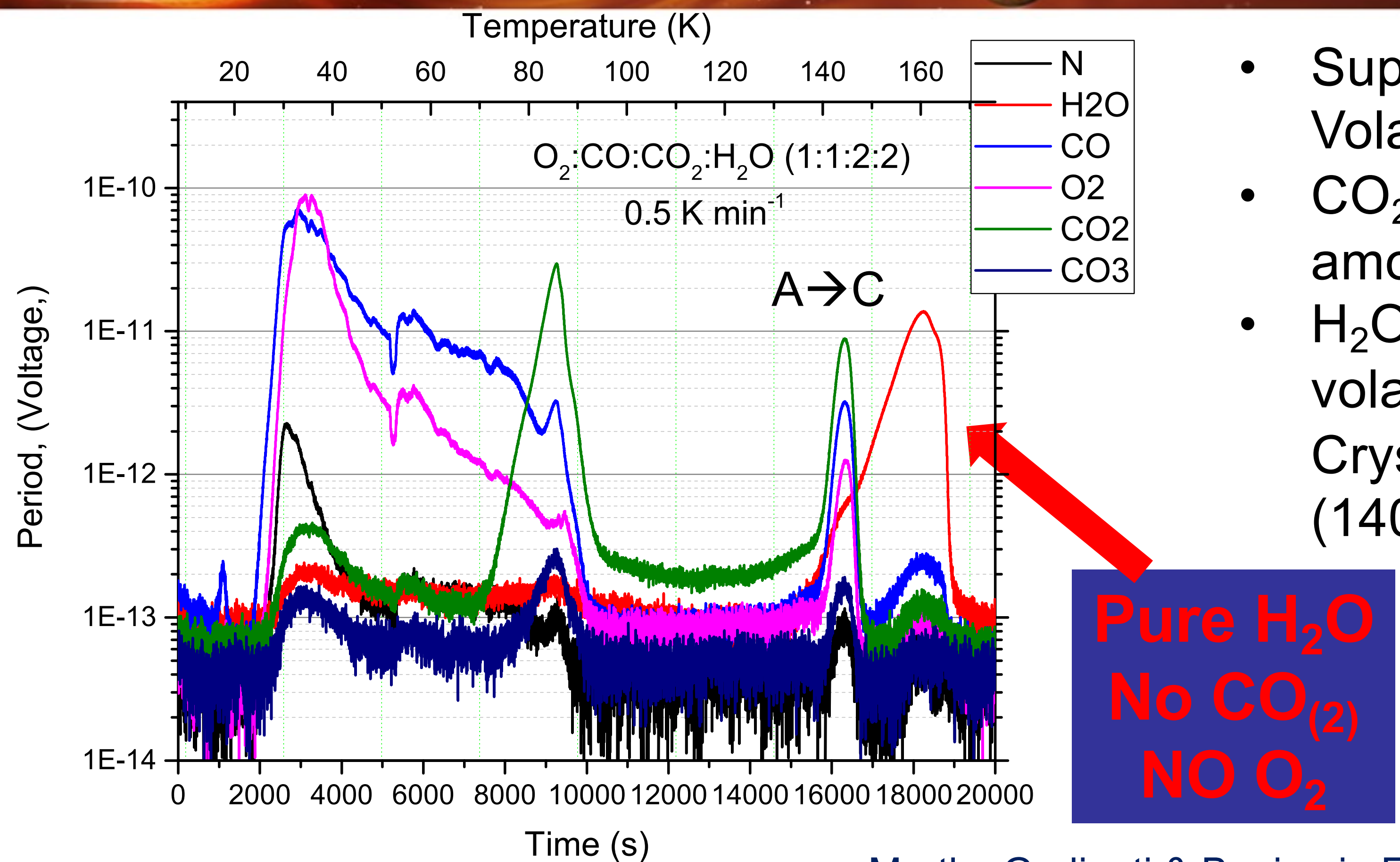


NIST e-impact Ionization of CO_2 gives ~10%CO ~10% O

Pure CO_2 No CO

Murthy Gudipati & Benjamin Fleury – To be Published

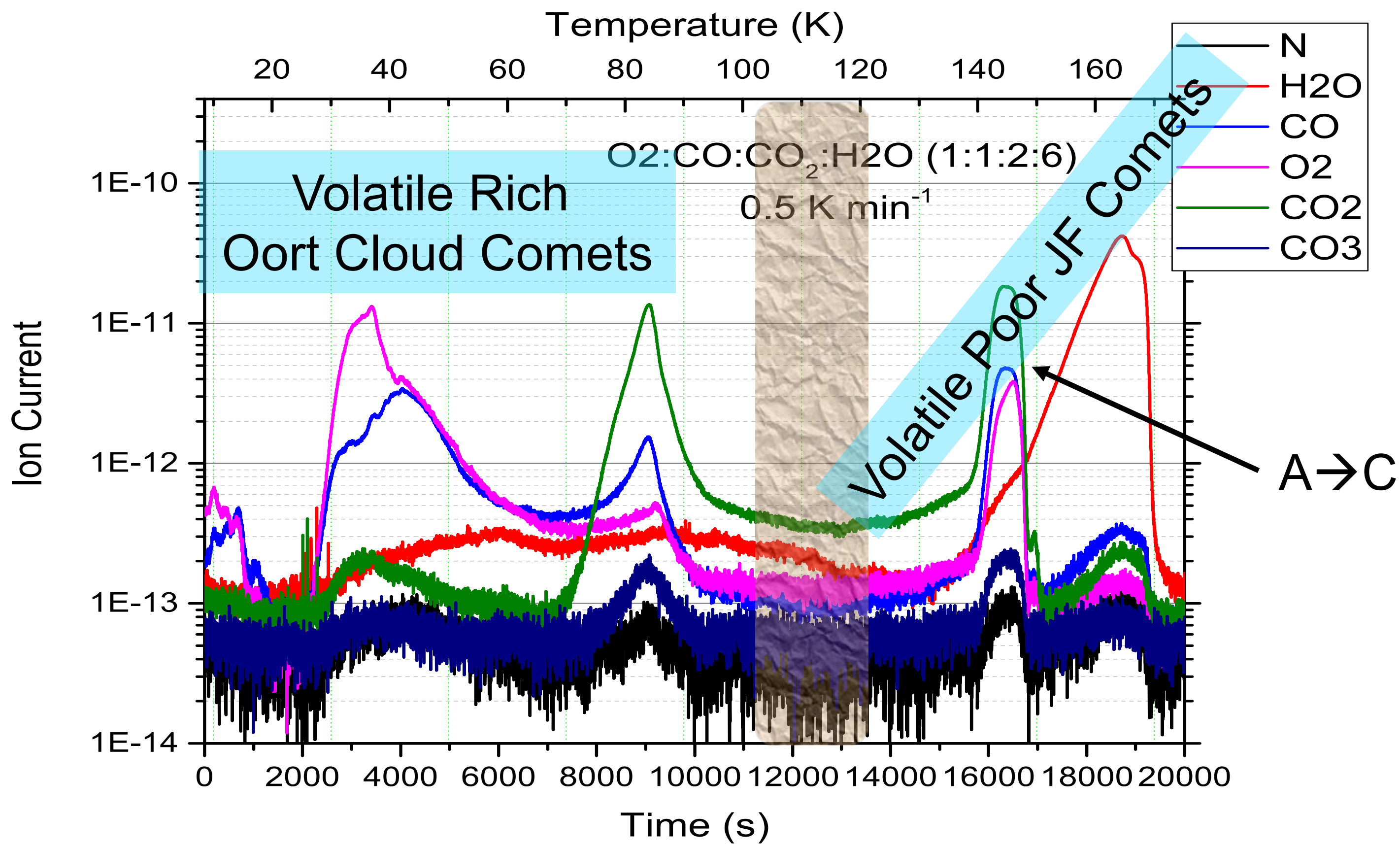
Outgassing of O_2, CO, & CO_2 in H_2O Ice



- Supervolatiles trap Volatiles
- CO_2 traps small amounts
- H_2O expels ALL volatiles at Amorph → Crystalline transition (140 K)

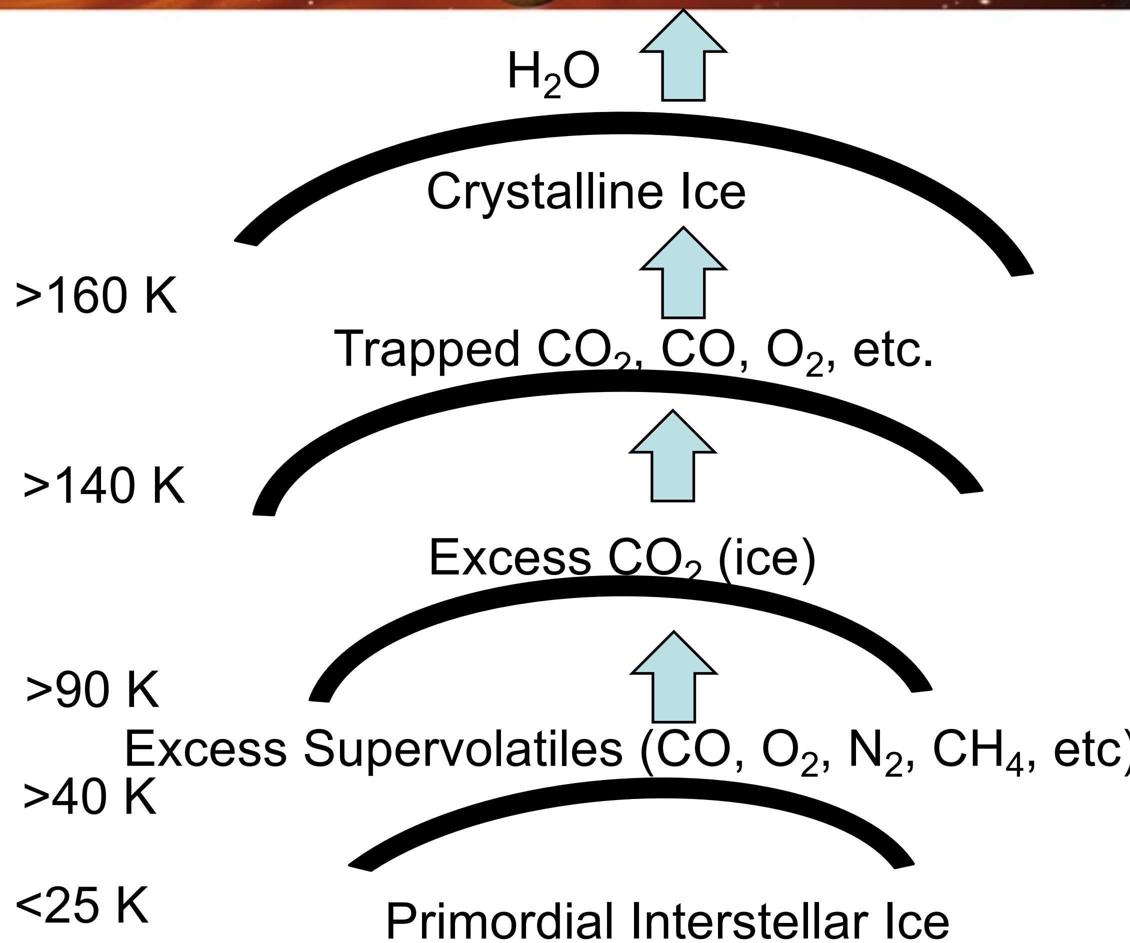
Murthy Gudipati & Benjamin Fleury – To be Published

Volatile Depleted vs. Volatile Rich Comets



Murthy Gudipati & Benjamin Fleury – To be Published

Thermal Gradients and Volatile Production



Part I: Conclusions

We need more Spectroscopic Observations (JWST?) of condensed phase Protoplanetary Disk at high spatial resolution!

Tracers that lead us all the way back to the Solar System formation.

- Amorphous H_2O Ice
- $CO_{3;}$ O_3?
- S_2, D_2O, $^{14}N/^{15}N$, ?? (not discussed here)

Thermal Evolution of Amorphous Ice Composition is Complex

- Determined by CO_2 concentration
- Determined by maximum temperature conditions
  - <25 K – Primordial – Supervolatile Rich (CO, N_2, O_2, CH_4, Ar, etc.)
  - <100 K – CO_2 depleted
  - <120 K – Amorphous
  - >140 K – Volatile depleted & Crystalline.

Part II: Habitability in Evolved Solar Systems

Habitability is necessary but not sufficient for Astrobiology

Is there Life in Our Solar System beyond Earth?
Which environments are Habitable?
“Ocean Worlds” – Europa, Enceladus, Titan, etc…

Complex Organic Molecules (COMs) in Enceladus Oceans

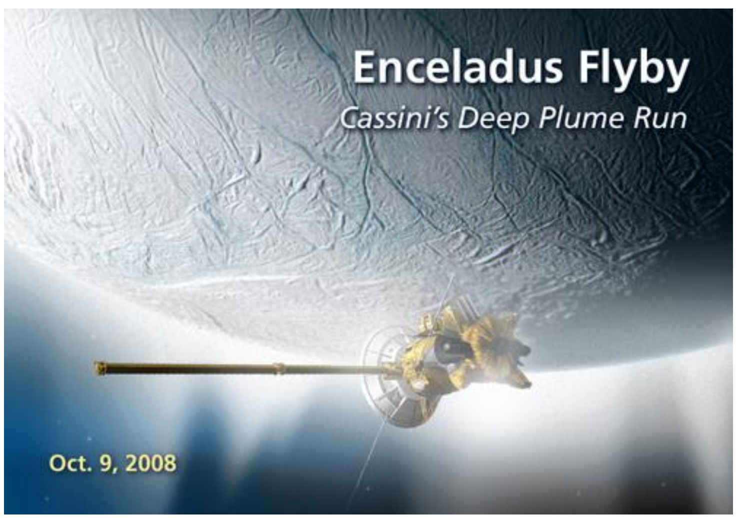
LETTER

Nature 558 (2018) 564-568

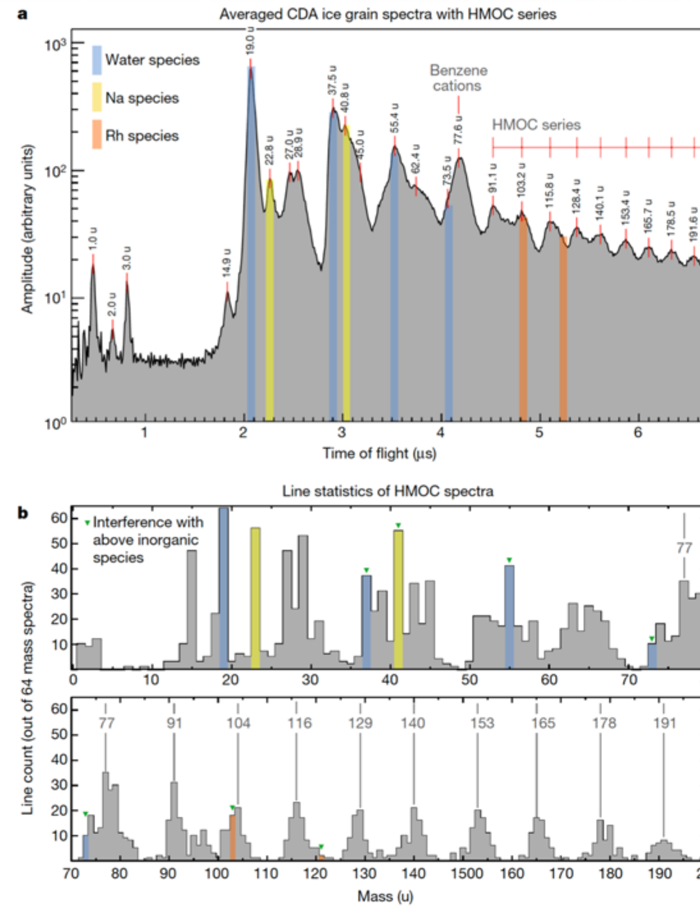
https://doi.org/10.1038/s41586-018-02

Macromolecular organic compounds from the depths of Enceladus

Frank Postberg[1,2,3,13]*, Nozair Khawaja[1,13], Bernd Abel[4], Gael Choblet[5], Christopher R. Glein[6], Murthy S. Gudipati[7], Bryana L. Henderson[7], Hsiang-Wen Hsu[8], Sascha Kempf[8], Fabian Klenner[1], Georg Moragas-Klostermeyer[9], Brian Magee[6,8], Lenz Nölle[1], Mark Perry[10], René Reviol[1], Jürgen Schmidt[11], Ralf Srama[9], Ferdinand Stolz[4,12], Gabriel Tobie[5], Mario Trieloff[1,2] & J. Hunter Waite[6]

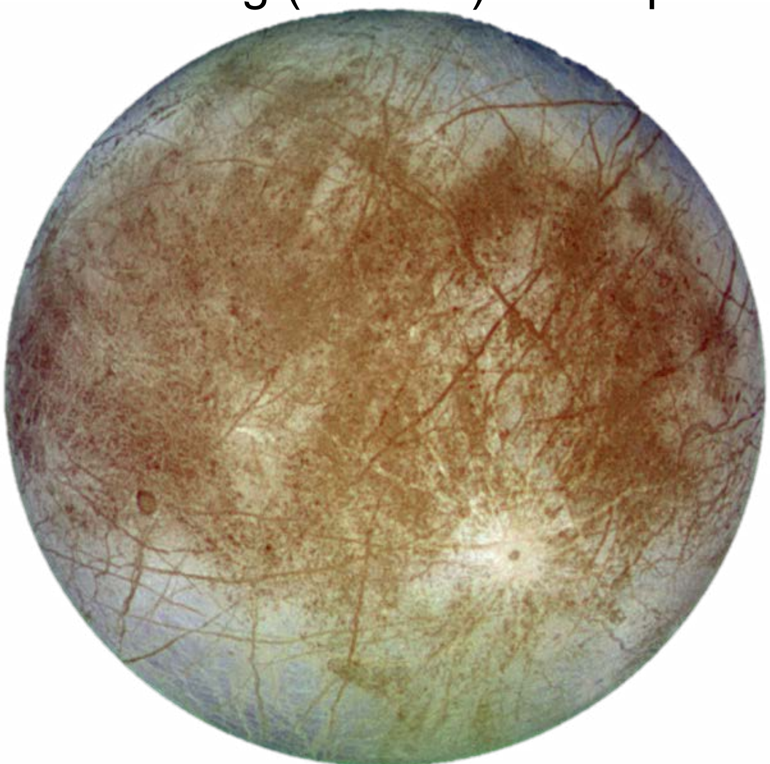


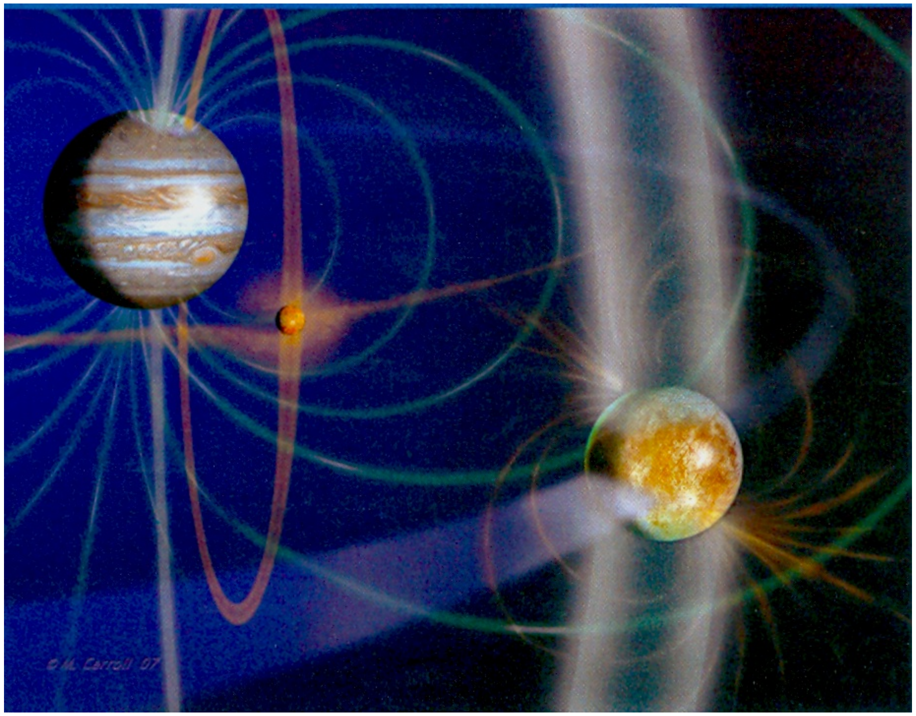
Enceladus has subsurface Ocean (Liquid Water) and Plumes eject Ocean material into Saturn's Rings



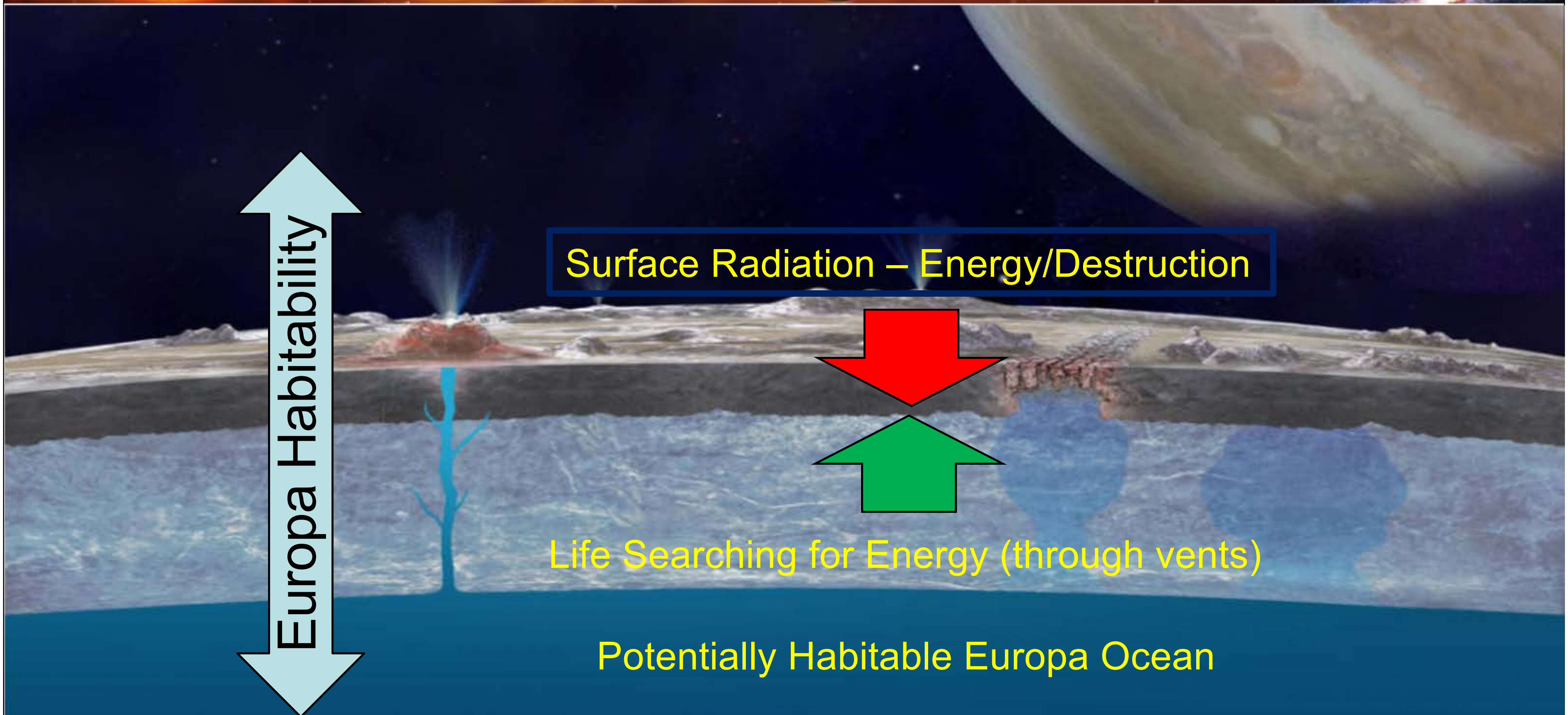
Ocean World Europa – Radiation & Habitability

Electrons, Protons, and Ions from Jupiter's Magnetosphere Reach Europa's Surface.
Electrons penetrate the deepest into Europa's surface:
Trailing (colored) Hemisphere **<25 MeV**; Leading Hemisphere: **>25 MeV**





Does Radiation Provide Energy for Habitability in Europa?

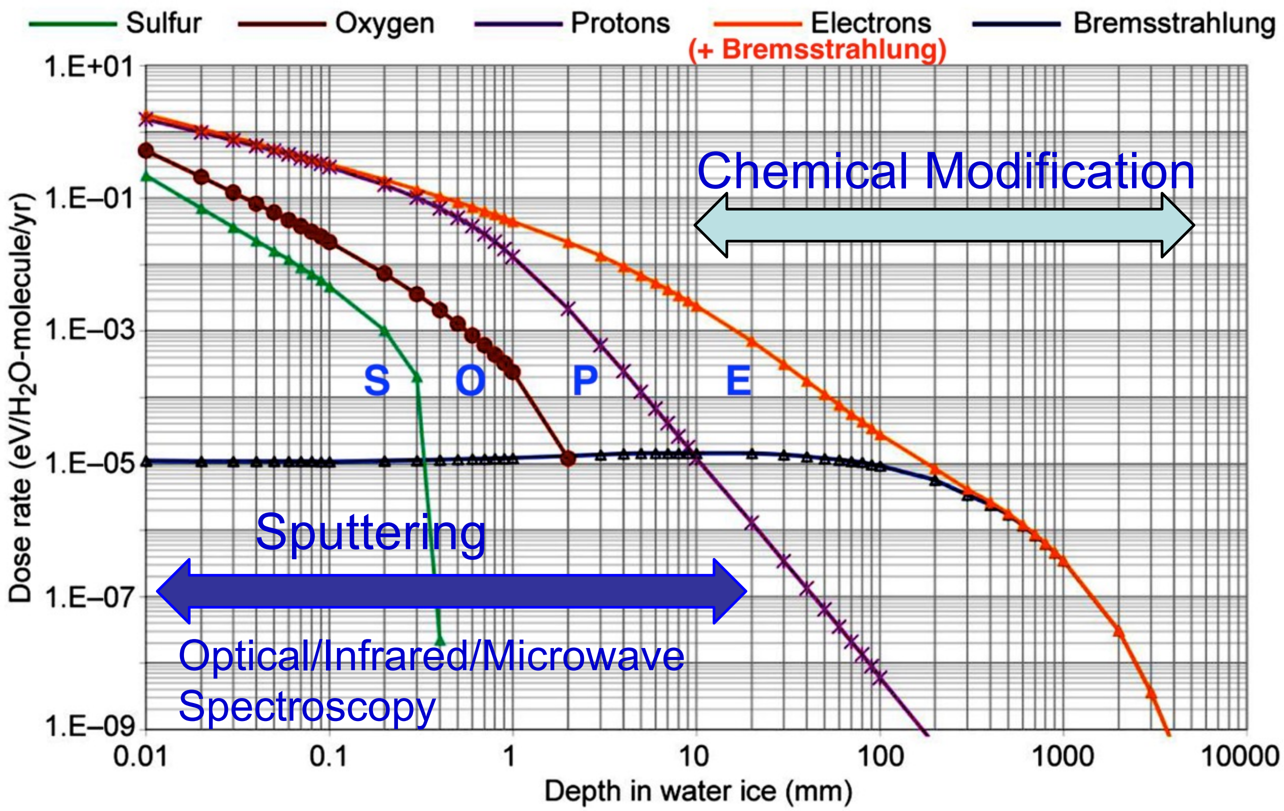


Modeling Europa's Radiation Dose

Based on liquid water or empirical data – no lab data YET published

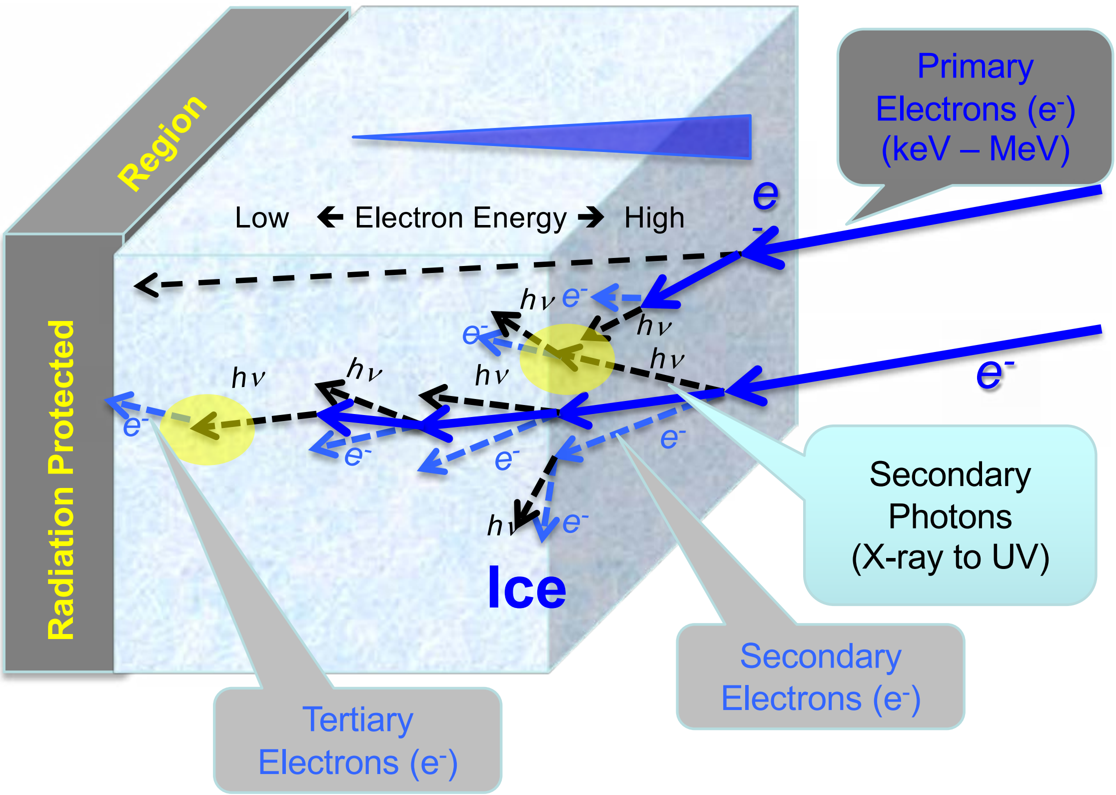
Electrons(compared to Protons and ions) penetrate the deepest into materials.

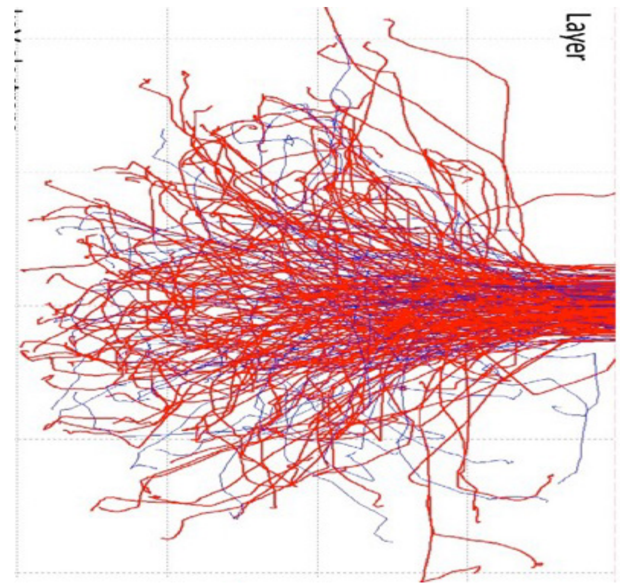
Bremsstrahlung (X-rays) produced by Electrons in matter penetrates even deeper.



Plot from: Paranicas et al. (2002)

Electron Impact on Matter: Primary and Secondary Radiation

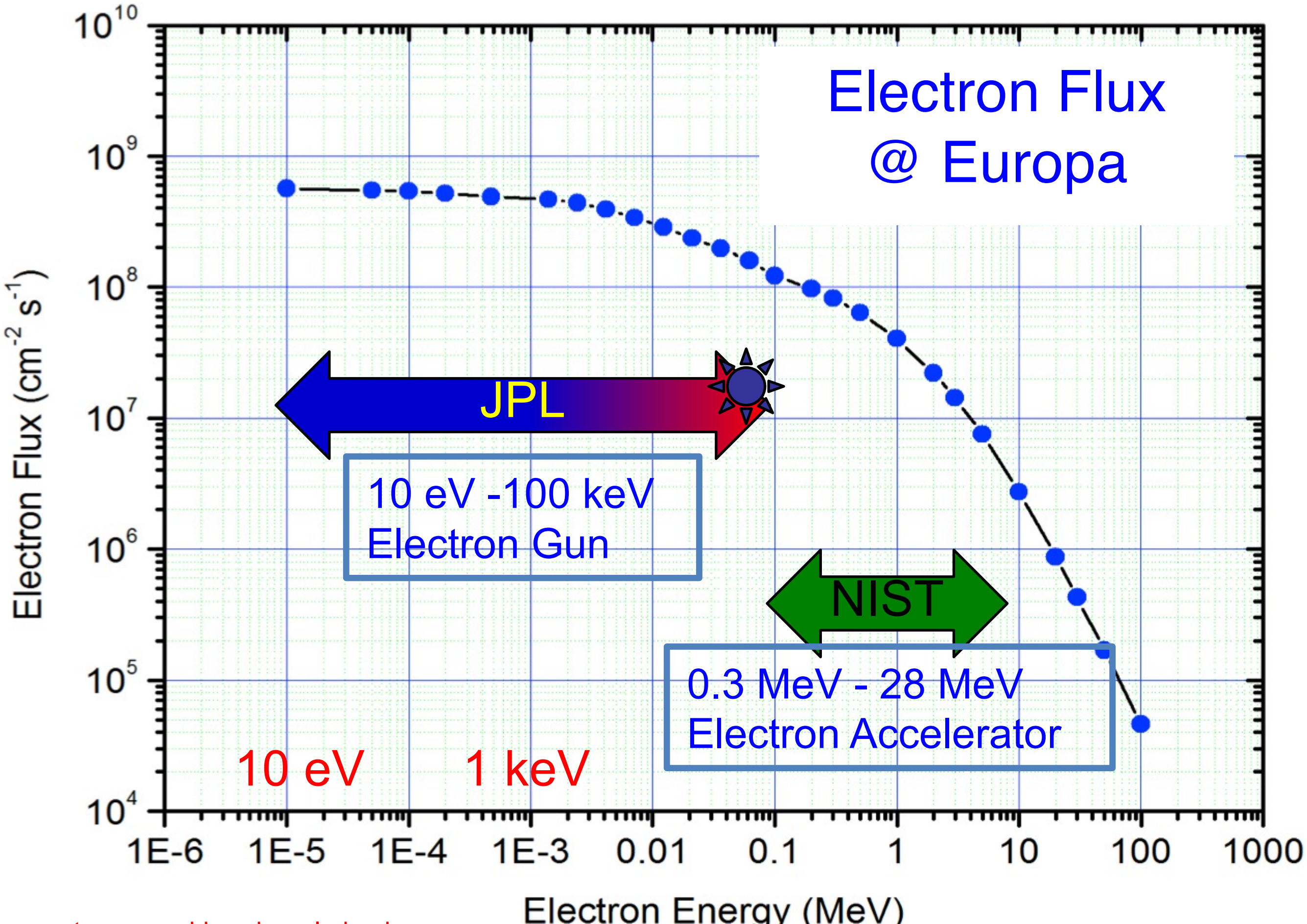




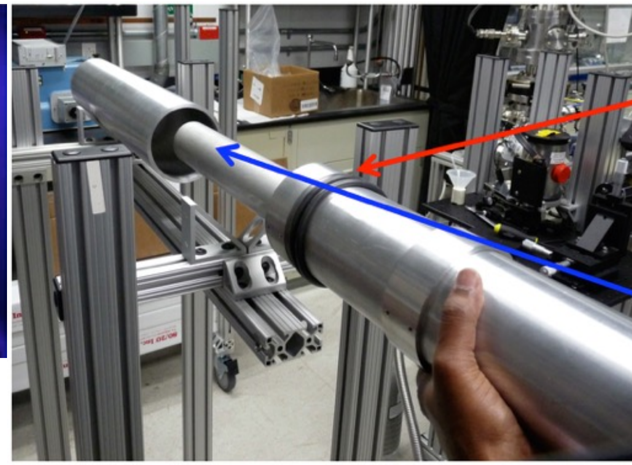
Electron Trajectory Simulation Through Materials

Present Capabilities of the ISL @ JPL

Europa's
Trailing-Leading
Cutoff
20 MeV?
25 MeV?



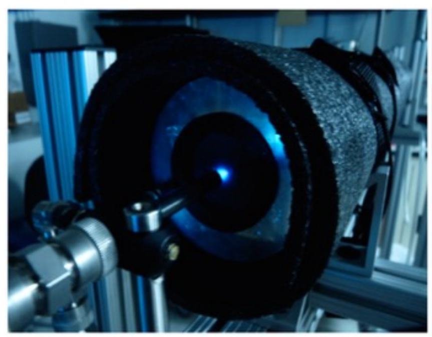
Ice Chamber for Europa’s High-Energy Electron And Radiation-Environment Testing



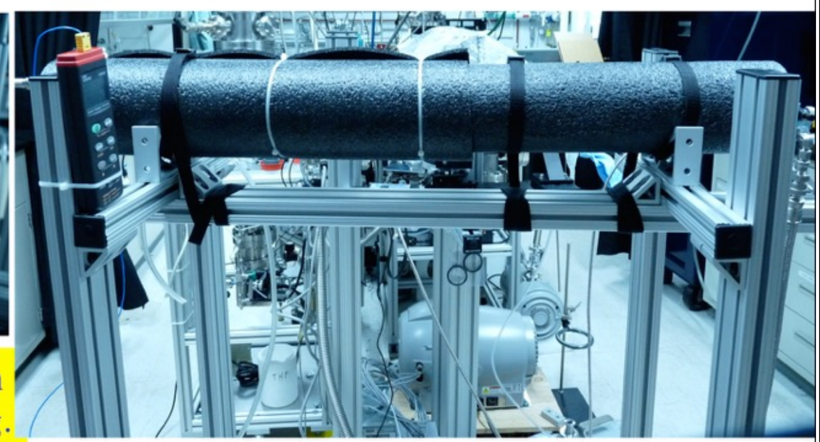
Outer Telescope with vacuum seal O-rings.

Inner 2.5-inch diameter tube for water ice frozen in the tube or loaded as crushed powder.

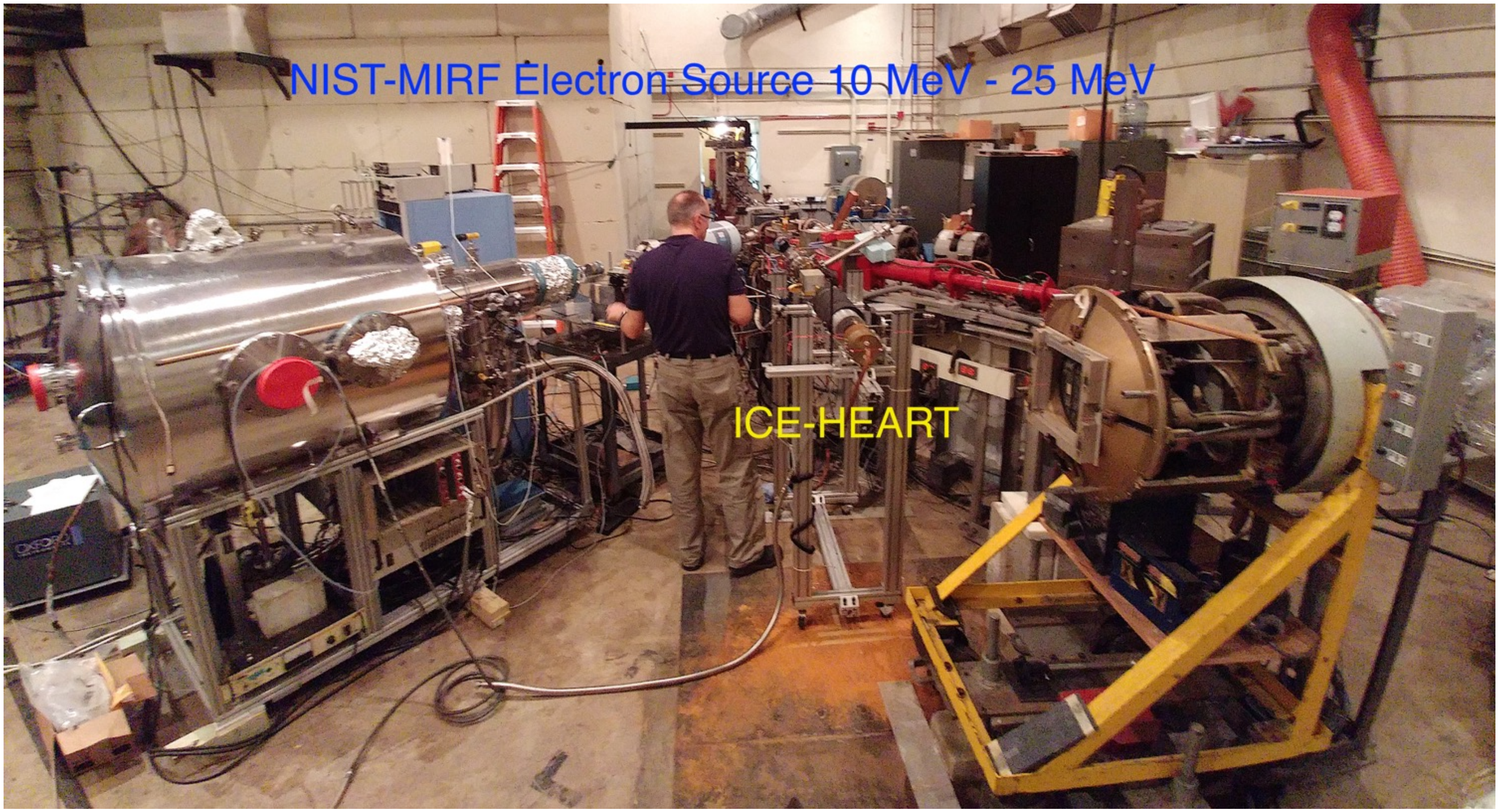
(ICE-HEART)
~100 K and >
~ 1cm – 100 cm



Insulated for 100 K operation
Using liquid nitrogen cooling.



NIST Electron Sources Cover 300 keV to 28 MeV



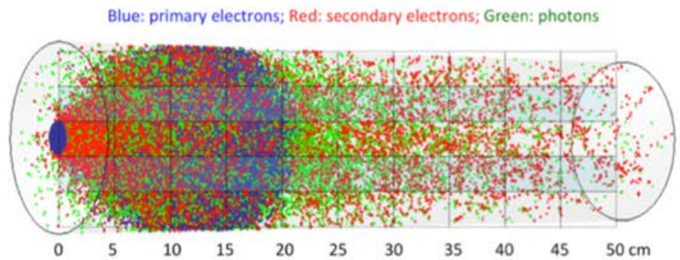
ICE-HEART Crew in Action @ NIST MIRF

Ice Sample Handling in (subsequent to) High-Radiation Environment

How to Quantify Bremsstrahlung (X-rays)?

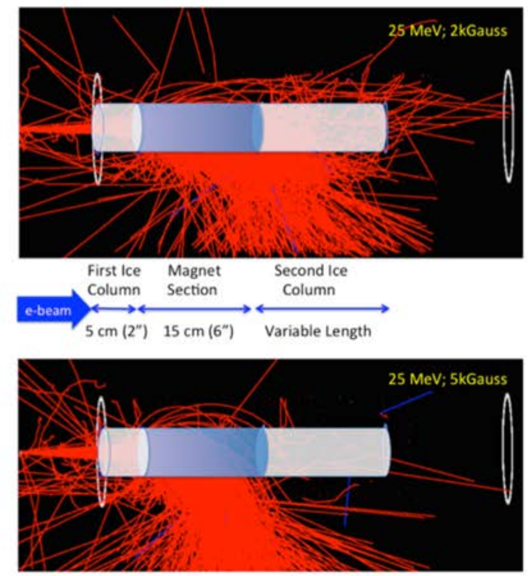
By Removing Secondary Electrons

5kG Halbach Cylindrical Magnet @ 80 K Deflecting Primary and Secondary Electrons Enables Quantification of X-ray Yields and Penetration Depths



Above: typical secondary particle generation in the ICE-HEART when high energy electrons impinge upon ice with no magnet.

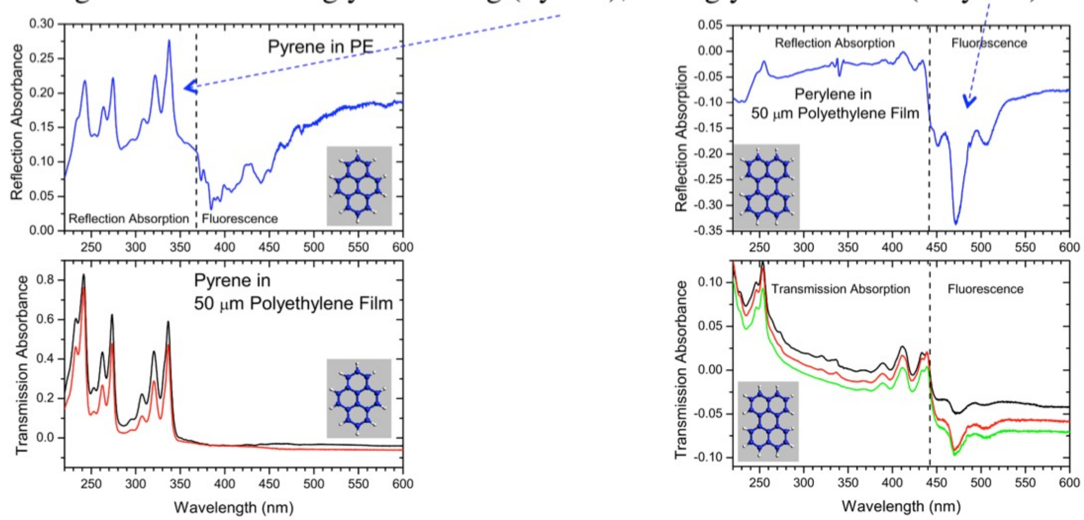
Right: Inserting a strong SmCo magnet (5 kGauss) into the chamber causes electrons to be deflected to the side, so that they no longer impinge upon the detector.

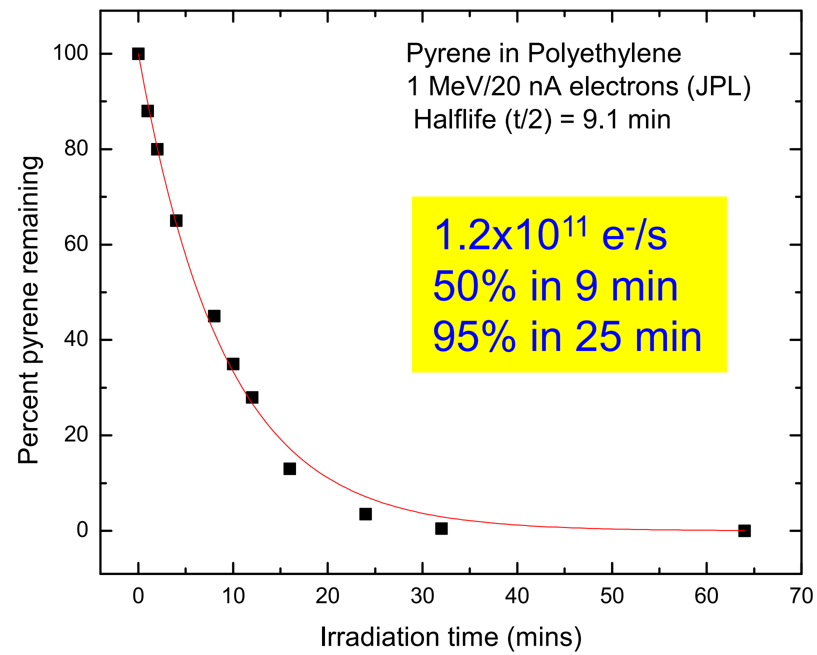


Organic (PAH) Damage by 1MeV Electrons

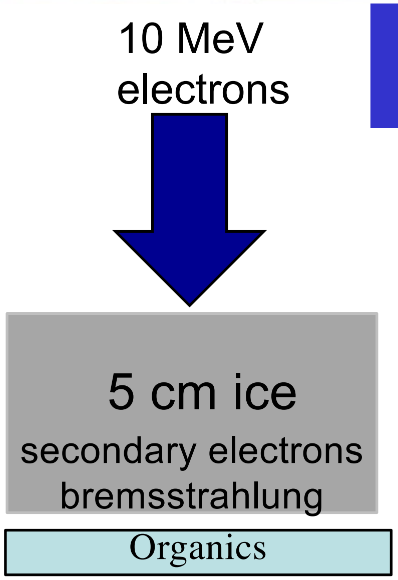
UV-VIS Absorption Spectra of PAHs In Polyethylene Film

Two Organic Probes: Strongly Absorbing (Pyrene); Strongly Fluorescent (Perylene)



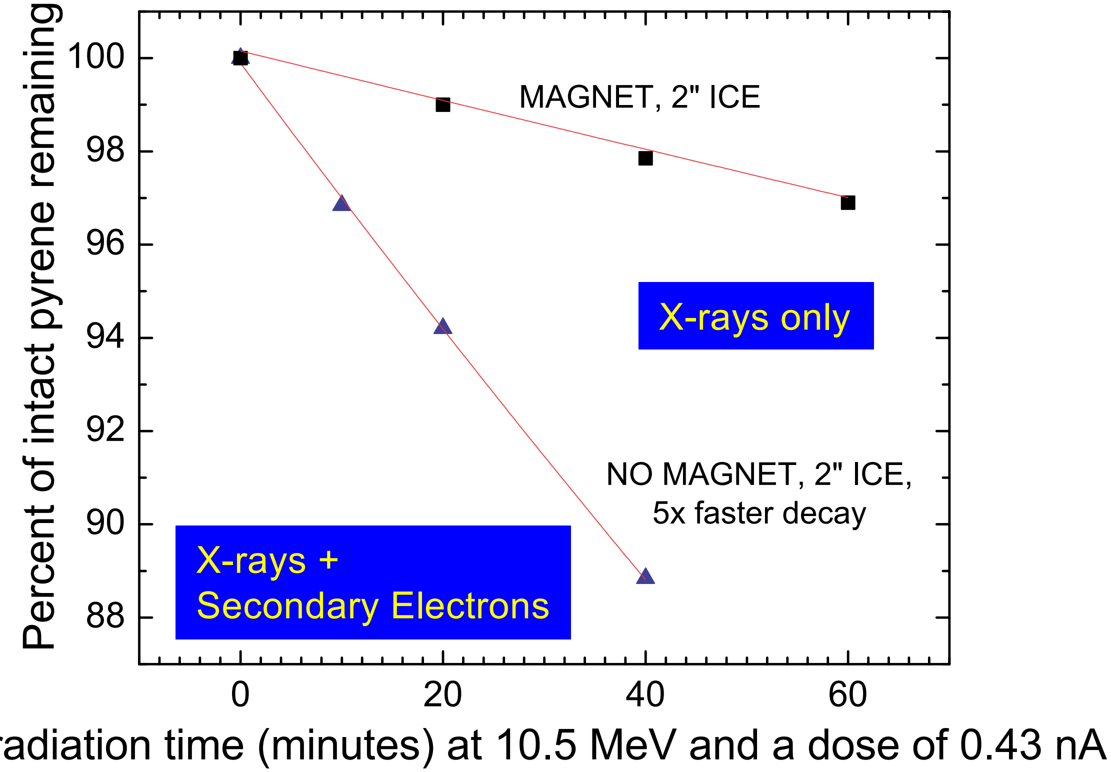


Secondary Electrons vs. X-rays



Damage by Electrons 80%
X-rays 20%

First JPL-NIST MIRF Data for 10 MeV Primary Electrons bombarding 5 cm thick ice targets at 100 K

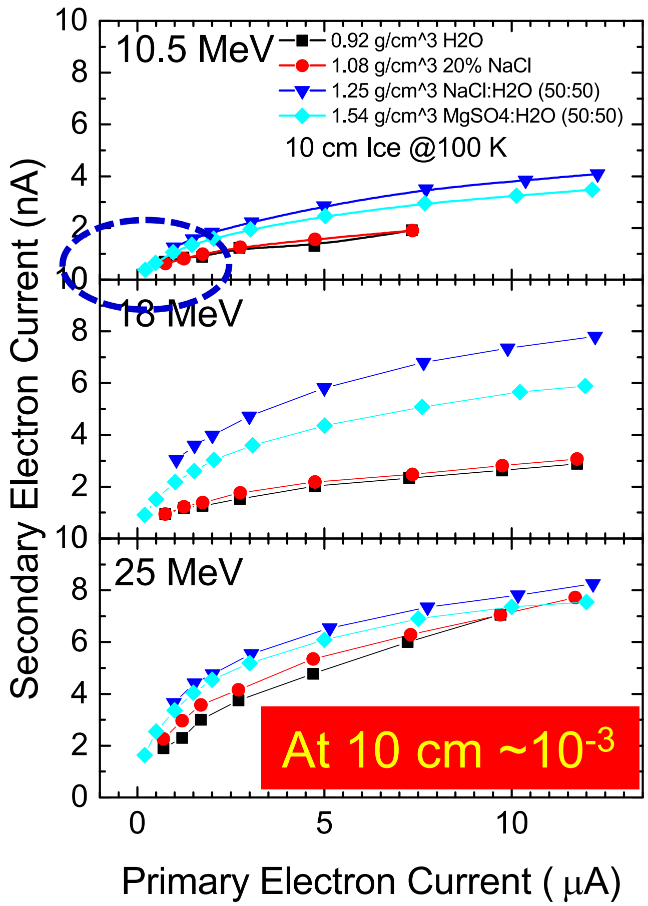


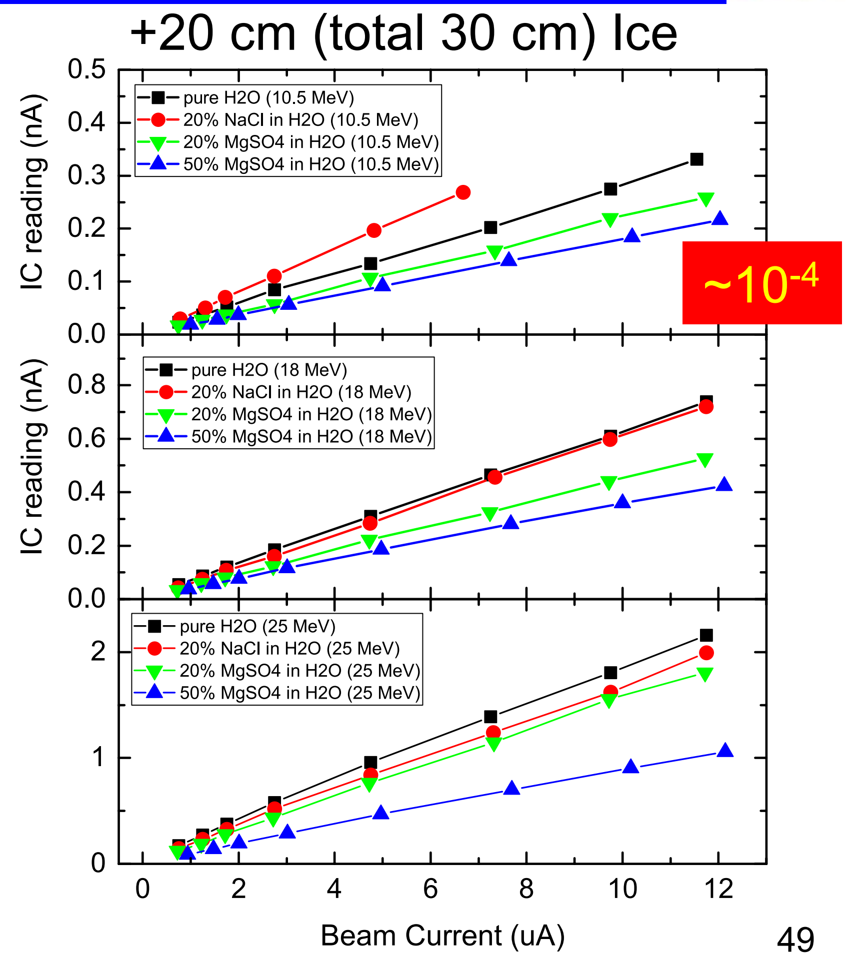
Europa Ice Analogs (10 cm) with NaCl & $MgSO_4$

Electrons @ 10 cm

Bremsstrahlung @ 30 cm

Electrons:
0.1 % @ 10 cm
X-rays:
<0.01% @ 30 cm





Part II: Conclusions

- Solar System Ocean Worlds Such as Enceladus harbor Complex Organic Molecules.
- Europa Radiation can Sustain Life and Destroy Life as well.
- We do not yet know whetherLife exists on Europa in deep Ocean.
- Europa’s surface may not be Habitable up to one meter beneath the surface.

Postdoctoral Opportunities at ISL @ JPL

We are Always Open to Outstanding Laboratory Experimentalists: Post-Doctoral, Visiting Students (and Faculty) @ Ice Spectroscopy Lab

ISL Team (continued)

Acknowledgments

Thank You & Sapporo
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